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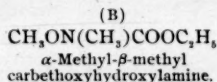
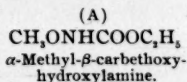
TWO ISOMERIC α,β -DIALKYL HYDROXYLAMINES.

I. α -METHYL- β -ETHYLHYDROXYLAMINE.

II. α -ETHYL- β -METHYLHYDROXYLAMINE.

BY LAUDER W. JONES.

In a previous article,¹ I described the products obtained by the action of methyl iodide, or of ethyl iodide, upon the sodium salt of carbethoxyhydroxylamine (oxyurethane), $\text{HONHCOOC}_2\text{H}_5$. With methyl iodide, two substances were formed:



These two compounds were separated easily by the action of a dilute solution of sodium hydroxide upon an ether solution containing them; the former (A), an acid, was extracted by

¹ THIS JOURNAL, 20, 38.

the alkali, while the latter (B) had no acid properties, and was left in the ether. Substance (A) could be isolated from the alkaline solution which contained its salt, by means of dilute sulphuric acid and ether.

From substance A by the action of concentrated hydrochloric acid at 100° , α -methylhydroxylamine hydrochloride was formed, while substance B, by similar treatment, gave α -methyl- β -methylhydroxylamine hydrochloride. When substance A was treated with sodium ethylate and methyl iodide it was converted into substance B.

These experiments suggested the possibility of making mixed α,β -dialkylhydroxylamines by introducing into carbethoxyhydroxylamine (oxyurethane) two different alkyl groups one after the other. There is, at present, only a single representative¹ of this class of compounds described in the literature, although a few mixed β,β -dialkylhydroxylamines have been prepared.

I.

The Preparation of α -Methyl- β -ethylcarbethoxyhydroxylamine,
 $\text{CH}_3\text{ON}(\text{C}_2\text{H}_5)\text{COOC}_2\text{H}_5$.

When α -methyl- β -carbethoxyhydroxylamine (A), dissolved in alcohol, was treated with the calculated amount of sodium ethylate, and the equivalent amount of ethyl iodide was added, a reaction commenced at once, which was practically ended in the course of two days. Thus 19 grams of α -methyl- β -carbethoxyhydroxylamine with sodium ethylate and 25 grams of ethyl iodide gave a dense deposit of sodium iodide. This was removed, and the alcoholic solution was concentrated under diminished pressure until a small volume of liquid was left. This residue was mixed with water and extracted repeatedly with ether. The slight quantity of iodine which colored the ether was taken out by shaking the ether with a solution of sodium thiosulphate. To remove any unchanged monomethyl derivative (A), the ether was treated

¹ Behrend and Leucks: Ann. Chem. (Liebig), **257**, 237. By the action of ethyl bromide upon α -benzylhydroxylamine, these authors obtained a mixture of α -benzyl- β -ethylhydroxylamine hydrobromide and α -benzyl- β -diethylhydroxylamine hydrobromide, from which α -benzyl- β -ethylhydroxylamine could be isolated.

several times with a dilute solution of sodium hydroxide. From the ether, after it had been dried, I obtained, by distillation, a colorless, neutral oil (16 grams), with a peculiar, rather unpleasant odor, a little like that of amyl alcohol. Under atmospheric pressure it distilled, without decomposition, at 165° – 166° .

The Action of Concentrated Hydrochloric Acid upon α -Methyl- β -ethylcarbethoxyhydroxylamine.

α -Methyl- β -ethylhydroxylamine Hydrochloride, $\text{CH}_3\text{ONC}_2\text{H}_5\text{H}_2\text{Cl}$.—The neutral oil just described was quite readily decomposed by concentrated hydrochloric acid. Ten grams of it were heated with 20 cc. of acid in a sealed tube, at 100° , for about 8 hours. When the tube was opened, carbon dioxide and ethyl chloride escaped. The acid solution was evaporated over a water-bath until the hydrochloride remained as a thick oil. This solidified in the course of a day to a mass of colorless, granular crystals. This salt was so extremely deliquescent that it was difficult to make any satisfactory melting-point determination; it was found to be approximately 46° – 47° . Upon mixing an alcoholic solution of it with platinic chloride and ether, the corresponding chlorplatinate separated as a granular, orange salt, which melted with decomposition, at 174° – 175° .

0.1205 gram substance gave 0.0415 gram Pt.

Pt	Calculated for	Found.
	$(\text{CH}_3\text{ONC}_2\text{H}_5\text{H}_2)_2\text{PtCl}_6$	
	34.79	34.52

α -Methyl- β -ethylhydroxylamine, $\text{CH}_3\text{ONHC}_2\text{H}_5$.—This hydrochloride was treated with a solution of sodium hydroxide and distilled in such a manner that the vapor could be passed through a tube filled with pieces of solid sodium hydroxide, heated to 100° , and then condensed. The free dialkylhydroxylamine was found to be a colorless liquid, with a rather sweet, basic odor, not distinctly ammoniacal. It dissolved easily in water to form a solution which had a strong alkaline reaction, but did not reduce silver nitrate. The boiling point was 60° – 61° .

II.

The Action of Methyl Iodide upon α -Ethyl- β -carbethoxyhydroxylamine.

α -Ethyl- β -methylcarbethoxyhydroxylamine,
 $C_2H_5ONHCH_2COOC_2H_5$.—By the action of sodium ethylate and ethyl iodide upon carbethoxyhydroxylamine (oxyurethane), I previously¹ obtained two substances. One of them, the acid, was found to be α -ethyl- β -carbethoxyhydroxylamine, $C_2H_5ONHCOOC_2H_5$. When this compound reacted with methyl iodide, in an alcoholic solution which contained the calculated amount of sodium ethylate, considerable heat was evolved, and the separation of sodium iodide commenced at once. Two days later the action was complete. After most of the alcohol had been removed by distillation, the residual liquid was poured into water and extracted a number of times with ether. The ether extract, first washed several times with a dilute solution of sodium hydroxide, was finally dried and distilled. A colorless, neutral oil which boiled at 166° – 167° was obtained. This oil, like its isomer described above, possessed a peculiar odor resembling fusel oil, and vaguely suggesting that of an isocyanide.

The Action of Concentrated Hydrochloric Acid upon α -Ethyl- β -methylcarbethoxyhydroxylamine.

α -Ethyl- β -methylhydroxylamine Hydrochloride, $C_2H_5ONHCH_2H_2Cl$.—By heating 8 grams of this neutral oil, b. p. 166° – 167° , with concentrated hydrochloric acid for several hours, in a sealed tube, at 100° , it was decomposed with the formation of carbon dioxide, ethyl chloride, and the hydrochloride of the dialkylhydroxylamine. This salt was easily soluble in boiling chloroform, and could be precipitated almost completely from such a solution by the addition of dry ether. It crystallized in delicate, fibrous needles, which melted at 74° – 75° , and were not in the least deliquescent. The chlorplatinate which separated from an alcoholic solution, was a crystalline, orange powder that melted at 170° – 171° with decomposition.

¹ THIS JOURNAL, 20, 45.

0.2374 gram substance gave 0.0822 gram Pt.

Pt	Calculated for (C ₂ H ₅ ONCH ₃ H ₃) ₃ PtCl ₃	Found.
	34.79	34.62

α -Ethyl- β -methylhydroxylamine, C₂H₅ONHCH₃—The hydrochloride was decomposed by heating it with a solution of sodium hydroxide; the vapors were dried and condensed. The free dialkylhydroxylamine was a colorless liquid with an odor similar to that of the isomer. Its boiling point was 65°-65°.5, a little higher than that of the isomeric α -methyl- β -ethylhydroxylamine.

Several methods suggest themselves as practical for the preparation of the third isomeric hydroxylamine, β -methyl- β -ethylhydroxylamine, C₂H₅NCH₃OH. It might be formed by the careful oxidation of methylethylamine with hydrogen peroxide, according to the method employed by Dunstan and Goulding¹ for preparing β,β -dialkylhydroxylamines from secondary amines. It might be obtained more easily by treating nitromethane with zinc methyl. The "triethylamine oxide" described by Bewad,² and prepared by the action of nitroethane upon zinc ethyl, has turned out to be β -ethyl- β -butylhydroxylamine,³ CH₃CHC₂H₅.NC₂H₅OH.

In a similar manner β -methyl- β -ethylhydroxylamine, CH₃CH₂NCH₃OH, should result when nitromethane is acted upon by zinc methyl. These methods are now being tried.

It will be of some interest to study these three isomeric alkyl hydroxylamines, and other similar ones containing various alkyl groups, with respect to the electrical conductivities of their water solutions. I intend to study them from this standpoint.

¹ J. Chem. Soc., **75**, 1010. Mamlock and Wolfenstein: Ber. d. chem. Ges., **33**, 159.

² J. Russ. Phys. Chem. Soc., **30**, 125.

³ Bewad: J. Russ. Phys. Chem. Soc., **33**, 455; Dunstan: J. Chem. Soc., **70**, 641.

STUDIES IN CATALYSIS.

[FOURTH COMMUNICATION ON CATALYSIS.]

BY S. F. ACREE AND J. M. JOHNSON.

Such reactions as the saponification of esters, and the hydrolysis of amides, nitriles, oximes, cane sugar, etc., by water, the formation of esters from acids and alcohols, and the rearrangement of acetylhalogenaminobenzene derivatives into halogen acetanilide derivatives¹ are accelerated by acids. The rate of transformation of the cane-sugar, esters and amides can be represented by the following equation:

$$\frac{dx}{dt} = KC_{sub} \times C_H \times C_{H_2O},$$

in which K is the saponification constant, C_{sub} the concentration in gram molecules per liter of the substance which is being hydrolyzed, C_H the concentration of the hydrogen ions and C_{H_2O} the concentration of the water, which in dilute water solutions is practically constant.

In the hydrolysis of amides² and oximes in dilute water solution the amide and oxime and also the hydrogen ions are used up and the reaction appears to be bimolecular. In the inversion of cane sugar and the saponification of esters in dilute aqueous solutions, however, the concentrations of the hydrogen ions and of the water are not appreciably changed and the reaction appears to be monomolecular.

Chemists³ have long known that we have not data sufficient

¹ Acree and Hinkins: *THIS JOURNAL*, **28**, 370; *Dental Cosmos*, June, 1901. Acree and Johnson: *THIS JOURNAL*, **37**, 410.

² Ostwald: *J. prakt. Chem.*, **135**, 1 (1883). Remsen and Reid: *THIS JOURNAL*, **31**, 284. Reid: *Ibid.*, **34**, 397.

³ Ostwald: *Z. physik. Chem.*, **34**, 248. Luther and Schilow: *Ibid.*, **46**, 777. Wegscheider: *Ibid.*, **34**, 290. Wagner: *Ibid.*, **28**, 33. Slaton: *Ibid.*, **45**, 512. Bray: *Ibid.*, **54**, 463. Kaufler: *Ibid.*, **55**, 502. Walton: *Ibid.*, **47**, 209. Brode: *Ibid.*, **37**, 290. Schilow: *Ibid.*, **43**, 641. Bredig and Ikeda: *Ibid.*, **37**, 1. Bredig and Walton: *Z. f. Elek. Chem.*, **9**, 117. Bredig and Stern: *Ibid.*, **10**, 585. Bredig: *Ibid.*, **11**, 528. Bredig and Haber: *Z. anorg. Chem.*, **17**, 284. Kastle and Loewenhardt: *THIS JOURNAL*, **24**, 491; *Ibid.*, **29**, 397, 563. Kastle: *Ibid.*, **27**, 481. Kastle and Clarke: *Ibid.*, **28**, 518. Kastle, Johnston and Elvove: *Ibid.*, **31**, 521. Kastle and Smith: *Ibid.*, **32**, 376.

to tell from the reaction constants whether in such reactions intermediate compounds are formed which are the substances really undergoing transformation. One school has held that in such catalytic reactions the catalyzer does not enter into combination with any substance present, but affects the velocity of the reaction much as a change of solvent does. Another school, however, believes that the velocities of some reactions are increased or decreased because the catalyzer enters into combination with some substance or substances present and the new complexes have reactivities different from those of the complexes from which they were formed. The object of the present paper is to discuss some of these reactions from this latter point of view.

In those reactions discussed in this communication it may be said that *"When a substance added to a solution in which a certain reaction is taking place causes an increase or decrease in the velocity of that reaction, without being itself altered at the end of the reaction, it does so because it unites to some extent with some compound or compounds present and causes an increase or decrease in the concentration of some substance taking part in the reaction, or because it forms some new substance (or substances) which yields the same end-products more or less readily than did the substances in the original solution. Of course, the solution conditions, such as volume, solvent, temperature, etc., must not be changed."*

ON THE REACTIONS BETWEEN THIURAZOLES AND ALKYL HALIDES.

Phenylthiourazole¹ and phenylurazole, and their salts react with alkyl halides and form esters. In a solution of an alkyl halide and phenylthiourazole there are present both molecular and ionized phenylthiourazole, and the velocity of the reaction might be proportional to the concentration of the urazole ions, or to that of the urazole molecules, or to both alike.

The reaction velocity would then be expressed by the equations:

¹ Acree: THIS JOURNAL, 27, 118; 31, 185; 32, 606; 37, 71, 361; 38, 1. Ber. d. chem. Ges., 35, 553; 36, 3139; 37, 184, 618.

$$\frac{dx}{dt} = KC_{urion} \times C_{alkyl\ halide}, \quad (1)$$

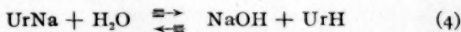
$$\frac{dx}{dt} = KC_{urmol\ salt} \times C_{alkyl\ halide}, \quad (2)$$

or

$$\frac{dx}{dt} = KC_{ur} \times C_{alkyl\ halide}, \quad (3)$$

depending upon whether the urazole ions, molecules, or both alike, react with the alkyl halide.

The salts are partly hydrolyzed,



and in a solution of a thiourazole salt and an alkyl halide the alkyl halide may react with the urazole ions, the molecular urazole salt or the free thiourazole formed from the salt by hydrolysis. The equations expressing these reactions are

$$\frac{dx}{dt} = KC_{urmol\ salt} \times C_{alkyl\ halide}, \quad (5)$$

$$\frac{dx}{dt} = KC_{urion} \times C_{alkyl\ halide}, \quad (6)$$

$$\frac{dx}{dt} = KC_{ur\ salt} \times C_{alkyl\ halide}, \quad (7)$$

$$\frac{dx}{dt} = KC_{ur\ acid} \times C_{alkyl\ halide}, \quad (8)$$

in which, as above, $C_{alkyl\ halide}$ represents the concentration in gram molecules per liter of the alkyl halide present at any moment, C_{urion} the concentration of the urazole ions, $C_{urmol\ salt}$ the concentration of the undissociated urazole salt, and $C_{ur\ acid}$ the concentration of the undissociated acid, and C_{ur} the total concentration of the urazole.

In order to decide between these possibilities it is evidently necessary to know the relative amounts of urazole ions and molecules and the actual velocity of the reaction. In the reaction between the phenyl thiourazole and the alkyl halide

there was found a gradual decrease in the value of the constant obtained by substituting the necessary data in the equation for the reaction of the second order $\frac{x}{t(A-x)} = AK$ and these constants were lowered very considerably by the addition of hydrochloric acid. It is evident that the halogen acid liberated in the reaction,

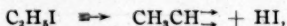


suppresses the ionization of the phenylthiourazole. Since the velocity constant of the reaction is also lowered, it would be suspected at once either that (1) the urazole ions are the product chiefly concerned in the reaction with the alkyl halide or (2) that the halogen acid reacts in some way with some of the substances present and lowers the reaction velocity because the product formed by the halogen acid and the other substance can not react so readily with the alkyl halide.

Since the addition of an alkali to the solution of the phenylthiourazole and the alkyl halide greatly increases the velocity of the reaction, and since the salts of such weak acids are more highly ionized than the acids themselves, it would be suspected at once that the urazole ions are the substances which are chiefly concerned in the reaction with the alkyl halide. But such a conclusion would be justified only in the case that absolute agreement is found between the velocity constants and the concentration of the ions. It may be stated once for all that such agreement has been found experimentally. The urazole ions react with the alkyl halides entirely in accordance with the demands of the above equations. If the other urazole groups are concerned in the reaction it is only to a minor extent. Messrs. Brunel, Johnson and Shadinger have found that various salts of the urazoles react with the alkyl halides entirely in accordance with what is known concerning the ionization, hydration, and ionic velocities of the salts in such solutions.

The velocity constant of the reaction and the ionization of the urazole are both suppressed by the addition of other substances having an ion in common with the urazole, whether

the urazole be in the form of the free acid or a salt. It has been found in general that alkyl halides react with the anions of hydroxides, carbonates, thiourazoles, urazoles, thioacetic acid and other substances. It should be stated that it has been definitely proved that our results are not in harmony with the hypotheses that the alkyl halides form alkyl derivatives (1) through intermediate dissociation into alkyl and halide ions, as Lobry de Bruyn and Steger¹ supposed, (2) through the union of the alkyl halide with cathions to form the cathion complexes $M \cdot IC_2H_5$ assumed by Euler,² (3) nor through the intermediate dissociation of the alkyl halides into a halogen acid and an unsaturated alkylene or alkylidene residue



assumed by Nef.³ The hypothesis might be advanced that in the reactions between alkyl halides and urazoles, hydroxides, carbonates, etc., the alkyl halide unites with the anion and forms a very unstable complex anion which immediately decomposes into iodide ions and an alkyl urazole, hydroxide or carbonate:



Such an assumption, however, is purely gratuitous and will be subjected to an experimental test.

It has been shown above, then, that acids, alkalies and salts influence the above reactions. Hydrochloric acid and hydroiodic acid act as negative catalyzers and lower the value of the velocity constant for the reaction between alkyl halides and phenylthiourazole, because the halogen acid suppresses the ionization of the phenylthiourazole, and hence causes a decrease in the concentration of the urazole ions, one of the two substances reacting according to equation (1). The addition of sodium hydroxide to the solutions of the phenylthiourazole and alkyl halide causes an increase in the velocity of the reaction because the sodium hydroxide reacts with the

¹ Rec. trav. Chim., **18**, 311.

² Ber. d. chem. Ges., **39**, 2726.

³ Ann. Chem. (Liebig), **298**, 202; **309**, 126; **310**, 316; **318**, 1, 137; **335**, 191.

phenylthiourazole and forms a sodium salt which furnishes the solution with a much greater concentration of urazole ions than does the free acid. Likewise, sodium iodide acts as a negative catalyzer, and lowers the velocity constant, for the reaction between sodium phenylthiourazole and ethyl iodide, because the sodium ions from the sodium iodide cause a suppression of the ionization of the sodium phenylthiourazole and a diminution of the concentration of the urazole ions.

The above work then shows that acids, bases and salts may act as negative or positive catalytic agents for certain reactions because they cause a change in the concentration of an intermediate product in the reaction. The intermediate product in the above reaction between phenylthiourazole and alkyl halides is the phenylthiourazole anion.

The following tables of work by Mr. G. H. Shadinger give a short resumé of some of the experimental results spoken of above. A large amount of work along these lines has been done by Messrs. R. F. Brunel, J. M. Johnson and G. H. Shadinger, which will be reported later in detail. The reaction was followed analytically by titrating the unchanged phenylthiourazole, or the sodium salt, with 0.1 N iodine solution. The solvent was 50 per cent alcohol and the solution was 0.05 N with respect to the phenylthiourazole, or sodium salt, and the ethyl iodide. The temperature was 50°. *T* gives the time in minutes and *A* the number of cc. 0.1 N iodine solution required to titrate 20 cc. of the solution at the beginning. *A* - *x* is the unchanged, and *x* the transformed urazole and ethyl iodide, expressed in cc. 0.1 N iodine. *AK* is the constant calculated for a bimolecular reaction, $AK = \frac{x}{t(A-x)}$, on the assumption that *A* is equal to 5 cc. 0.1 N iodine.

50°; 0.05 N 1-Phenyl-3-thiourazole; and 0.05 N ethyl iodide.

<i>T.</i>	<i>A.</i>	<i>A</i> - <i>x.</i>	<i>x.</i>	<i>AK.</i>
5	4.90	4.11	0.79	0.039
10	4.90	3.57	1.33	0.038
15	4.90	3.18	1.72	0.037
31	4.90	2.46	2.44	0.033
60	4.90	1.88	3.02	0.027
120	4.90	1.29	3.61	0.024
240	4.90	0.66	4.24	0.027

50°; 0.05 N 1-Phenyl-3-thiourazole; 0.05 N ethyl iodide; and 0.25 N HCl.

T.	A.	A-x.	x.	AK.
60	4.71	3.54	1.17	0.00584

The first table shows the constant decrease in the value of *AK* as the reaction proceeds, due to the increasing suppression of the ionization of the phenylthiourazole by the hydroiodic acid formed in increasing amount as the reaction proceeds. The second table shows very sharply the great decrease, caused by the 5 molecules of hydrochloric acid, in the ionization of the phenylthiourazole and the consequent decrease in the velocity constant of the reaction. The halogen acids act as negative catalyzers because they cause a decrease in the concentration of the urazole ions, and a consequent decrease in the velocity of the reaction.

50°; 0.1 N Sodium 1-Phenyl-3-thiourazole; and 0.1 N ethyl iodide.

T.	A'.	A'-x.	x.	A'K'.	AK.
10	9.44	3.80	5.64	0.156	0.0780
20	9.44	2.26	7.18	0.168	0.0840
40	9.44	1.30	8.14	0.165	0.0825
81	9.44	0.70	8.74 ^t	0.163	0.0815
190	9.44	0.30	9.14	0.169	0.0845

In this table *AK* represents the velocity which the reaction would have if the concentrations were the same as in the above reaction between the phenylthiourazole and ethyl iodide.

This table shows that the velocity constant for the reaction between the sodium thiourazole and the ethyl iodide is twice as great as that for the reaction between the phenylthiourazole and the ethyl iodide, because the sodium salt is more highly ionized. It was shown in other experiments that the addition of sodium iodide or sodium chloride to the solution causes a decrease in the velocity constant with the decrease in the percent of ionization of the sodium phenylthiourazole. The sodium iodide and sodium chloride act as negative catalyzers because they cause a decrease in the concentration of the urazole ions, and a consequent decrease in the velocity of the reaction.

The following table worked out by R. F. Brunel and J. M. Johnson¹ shows that potassium iodide acts as a negative catalyzer in the reaction between potassium 1-phenyl-4-methylurazole and ethyl iodide in 40 per cent alcoholic solution at 60°. The solutions are 0.3 N with respect to the ethyl iodide, potassium 1-phenyl-4-methylurazole, and the potassium iodide added. The second and third columns contain the percent of ethyl ester formed and the values of AK when no potassium iodide is added to the solution, while the fourth and fifth columns give the per cent of ester formed and the value of AK when one molecular quantity of potassium iodide is added to the solution. It is clear that the potassium iodide acts as a negative catalyzer because it causes a decrease in the per cent of ionization of the potassium 1-phenyl-4-methylurazole.

0.3 N Potassium urazole + 0.3 N ethyl iodide.			0.3 N Potassium urazole + 0.3 N ethyl iodide + 0.3 N potassium iodide.	
Time in hours.	Per cent reacted.	AK.	Per cent reacted.	AK.
0.5	18.00	0.44	12.9	0.30
1.0	30.35	0.45	23.9	0.31
2.0	48.20	0.46	40.0	0.33
4.0	62.85	0.42	52.9	0.28

ON THE REARRANGEMENT OF ACETYLHALOGENAMINO BENZENE DERIVATIVES INTO HALOGEN ACETANILIDE DERIVATIVES.

But even in some cases in which it is not easy to measure the small amounts of intermediate product present, it will be found possible to prove by the qualitative and quantitative study of the reactions that such are present.

Acetylhalogenaminobenzene² derivatives rearrange in the presence of halogen acids into halogen acetanilide derivatives,



but are stable in the presence of alkalis. The reaction is not appreciably reversible. That the reaction is not brought

¹ Acree: THIS JOURNAL, 37, 71.

² Slosson: Ber. d. chem. Ges., 28, 3265. Armstrong: J. Chem. Soc. 77, 1047. Chataway and Orton: *Ibid.*, 78, 1046; 77, 134; 79, 274; etc.

about by the mere presence of hydrogen ions¹ is shown by the fact that acetylchloraminobenzene in 16 per cent acetic acid solution at 0° is rearranged about 1,000 times as rapidly by hydrobromic acid of a given concentration as by hydrochloric acid in the same concentration. Furthermore, the acetic acid present in the solution furnishes 1.5 times as much hydrogen ions as the hydrochloric acid, but the velocity of rearrangement in the dilute acetic acid is very much smaller than when hydrochloric acid is present. Furthermore, a sample of pure acetylchloraminobenzene which stood several days under dilute sulphuric acid was recovered unchanged and 99 per cent pure, with the melting point 88°. Another proof that the rearrangement is not caused by the mere presence of hydrogen ions is furnished by the fact that acetylchloraminobenzene in ligroin is changed almost instantly by chlorine and bromine into parachloracetanilide or parabromacetanilide.

Still further proof that the rearrangement is not caused by the mere presence of the hydrogen ions, but involves the union of the hydrogen ions and halogen ions with the acetylchloraminobenzene is furnished by the order of the reaction and the qualitative and quantitative study of the course and nature of the reactions.

Blanksma² found that in the rearrangement of acetylchloraminobenzene by hydrochloric acid,

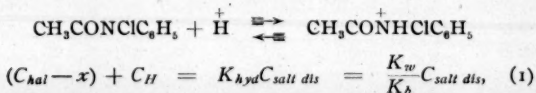


the velocity is proportional to the concentration of the acetylchloraminobenzene and to the *square* of the concentration of the hydrochloric acid. The concentration of the hydrochloric acid remains constant since it is not used up in the reaction. The constant obtained is that for a monomolecular reaction, which shows that the acetylchloraminobenzene is the only substance undergoing change in concentration. The fact that the reaction is monomolecular proves that the rearrangement is intramolecular and not intermolecular. If the reaction involved

¹ Acree and Johnson: *THIS JOURNAL*, **37**, 410.

² *Rec. trav. Chim.*, **21**, 366; **22**, 290.

the chlorination of the benzene nucleus in one molecule by the halogen amino group, or some derivative, of another molecule the reaction would be bimolecular, or of a higher order. This will be discussed in detail below. In nearly all catalytic reactions studied heretofore, such as the hydrolysis of esters, inversion of cane sugar, hydrolysis of amides, etc., the velocity of transformation has been found to be simply proportional to the concentration of the hydrogen ions. These two different cases are very important in that they throw light on the theory of catalysis in general and in that they make it possible to determine, in cases where only a small amount of the intermediate compound or salt is present, whether the substance undergoing transformation is the undissociated salt or the ionic form of the salt. The acetylchloraminobenzene is probably a very much weaker base than acetamide on account of the negative phenyl, acetyl and bromine groups attached to the nitrogen, and its salts will, therefore, be greatly hydrolyzed in aqueous solutions. Furthermore, the small amount of salt actually existing will be nearly completely dissociated in the extremely dilute solution. It follows then that the hydrolysis of the salt will follow the familiar equation of Arrhenius¹ and Walker,²

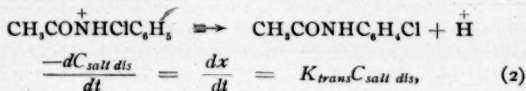


in which C_{hal} represents the original concentration, in gram molecules per liter, of the acetylhalogenaminobenzene derivative used, x the concentration of this substance changed into other products, including the complex salt, $(C_{hal} - x)$ the concentration of the acetylchloraminobenzene derivative at the moment equilibrium is established, C_H the concentration of the hydrogen ions, $C_{salt\ dis}$ the concentration of the complex cation, $\text{CH}_3\text{CONHCIC}_6\text{H}_5^+$, K_{hyd} the hydrolysis constant, K_w the ion product of water at the temperature, and K_b the

¹ Z. physik. Chem., 5, 1; 13, 407.

² *Ibid.*, 4, 319; 33, 137. J. Chem. Soc., 77, 5.

affinity constant of the weak base. The value of $C_{salt\ dis}$ can be calculated for all dilutions when K_b and the dissociation constant for the salt become known. K_b is too small to be measured accurately, by the methods now at hand, but this will be studied later. Since only a very small amount of the acetylchloraminobenzene and of the hydrogen ions are used up in forming the salt, $(C_{hal}-x)$ and C_H , are so nearly equal to the concentrations that these two would have if no salt were formed, that no appreciable error is involved in substituting for the values of $(C_{hal}-x)$ and C_H in equation (1) before any rearrangement occurs, the values of the concentrations that these two would have if either were alone in the solution. The same may be said for other cases considered below, as has been discussed by Walker, and this point will not be considered again. If the dissociated salt were the only substance rearranging into parachloracetanilide the rate of formation of the parachloracetanilide would be



in which K_{trans} is the velocity constant for the rearrangement of the dissociated salt which is present in the concentration $C_{salt\ dis}$. $-dC_{salt\ dis}$ is the small amount of $C_{salt\ dis}$ which rearranges in the time dt . $-dC_{salt\ dis}$ is exactly equal, in gram equivalents, to dx , the small amount of product formed by the rearrangement of the acetylhalogenaminobenzene. We may, therefore, write dx for the small amount of substance transformed, whether it be the intermediate compound or the acetylhalogenaminobenzene. The dx represents an increase and the $dC_{salt\ dis}$ a decrease; hence the one is the negative of the other.

In the total reaction, expressed by equations (1) and (2), we are dealing with two consecutive reactions. The first is a reversible reaction involving what may be considered practically a bimolecular and a unimolecular reaction. The second is a non-reversible bimolecular reaction. The concentration of

$C_{salt\ dis}$ at any moment depends upon the concentrations of the acetyl halogenaminobenzene, hydrogen ions, and anions, and upon the velocities of the two reactions. The first reaction is the neutralization of the base by an acid, and all such reactions take place, as a rule, immeasurably rapidly. The second reaction is, therefore, very slow in comparison with the first, and the equilibrium expressed in equation (1) is never appreciably disturbed by the change in the concentration of $C_{salt\ dis}$ in reaction (2). Hence according to (1)

$$C_{salt\ dis} = \frac{K_b}{K_w} (C_{hal} - x) \times C_H,$$

and equation (2) becomes

$$\frac{dx}{dt} = \frac{K_{trans} K_b}{K_w} (C_{hal} - x) \times C_H,$$

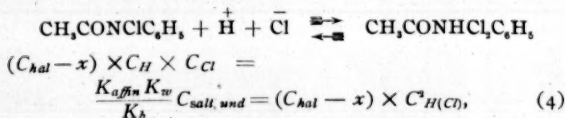
or

$$\frac{1}{C_H} \log \frac{C_{hal}}{(C_{hal} - x)} = \frac{K_b K_{trans}}{K_w} = K. \quad (3)$$

If the base existed entirely as salt the velocity of rearrangement would be K_{trans} ; but since only a small fraction of the base exists as salt, the reaction is retarded and the value of the constant actually obtained for the rate of transformation of the acetylchloraminobenzene is the value of the real velocity constant for the substance actually changing into the parachloracetanilide divided by the ratio of the amount of base to the amount of dissociated salt. But according to equation (3) this constant should be proportional to the concentration of the hydrogen ions. Experimentally, however, it is found that the constant varies as the square of the concentration of the hydrogen ions. It is, therefore, certain that the ion $CH_3CONHCIC_6H_5^+$ is not the substance which chiefly yields the parachloracetanilide, although it may do so to a very small extent. We must look elsewhere then for the substance which changes directly into parachloracetanilide.

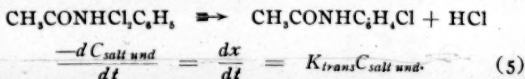
Since the amount of molecular salt present is very small, the formation of this undissociated salt will follow the require-

ments of the mass law as discussed above for the complex cathion and give equation (4)



in which K_{affn} is the dissociation constant of the salt, the molecular form of which has the concentration $C_{\text{salt und}}$.

If the undissociated salt yields the parachloracetanilide the rate of transformation of the acetylchloraminobenzene would be expressed by the equation



It is evident from (4) that instead of $C_{\text{salt und}}$ in (5) we can substitute

$$\begin{aligned} \frac{K_b}{K_w K_{\text{affn}}} (C_{\text{hal}} - x) \times C_{\text{H}} \times C_{\text{Cl}} \text{ or} \\ \frac{K_b}{K_w K_{\text{affn}}} (C_{\text{hal}} - x) \times C_{\text{H}(\text{Cl})}^2, \end{aligned}$$

and we then obtain

$$\begin{aligned} \frac{dx}{dt} &= \frac{K_{\text{trans}} K_b}{K_w K_{\text{affn}}} (C_{\text{hal}} - x) \times C_{\text{H}} \times C_{\text{Cl}} = \\ &\frac{K_{\text{trans}} K_b}{K_w K_{\text{affn}}} (C_{\text{hal}} - x) \times C_{\text{H}(\text{Cl})}^2, \end{aligned} \quad (6)$$

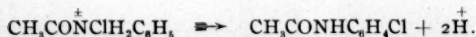
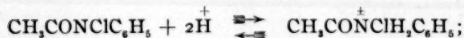
or

$$\frac{1}{t C_{\text{H}(\text{Cl})}} \log \frac{C_{\text{hal}}}{(C_{\text{hal}} - x)} = \frac{K_{\text{trans}} K_b}{K_w K_{\text{affn}}} = K.$$

But equation (6) expresses the results actually obtained experimentally. In other words, the velocity of the reaction shows that the substance undergoing change is the undissociated salt in (4) and not the cathion of this salt in (1). In

entire harmony with this is the fact that different acids (HCl, HBr, H_2SO_4 , CH_3COOH) do not give reaction constants bearing the relation to the concentration of their hydrogen ions demanded by equation (3). All of these acids would give the same complex cation in (1). The amount of this cation and consequently the rate of transformation of the acetylchloraminobenzene, should be strictly proportional to the concentration of the hydrogen ions, whatever the acid, if the reaction took place according to (1). Such, however, is not the case.

The fact that three different acids give different velocity constants is predicted by theory if equation (5) represents the method of change. The undissociated salts formed by all of these acids can be represented by $CH_3CONHClAcC_6H_5$ in which Ac represents the anion of the acid. These different salts would be expected to, and do, have different velocities of transformation as will be discussed below. Instead of the salt represented in the equation (4) another compound, to give a general illustration applicable in other cases as well as in the present one, could be formed by the addition of two anions or two cations to the acetylchloraminobenzene as follows:



This would lead to the same velocity constants as in equation (6) and as the present work does not decide absolutely between these two we shall confine our discussion of the case as if it took place according to equations (5) and (6) as it most probably does.

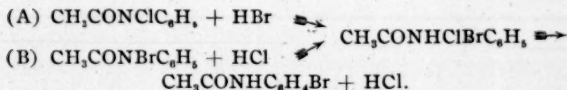
The quantitative evidence leads to the belief that acetylchloraminobenzene does not rearrange *per se* in the above reactions. The evidence further shows that the positive ion in equation (1), $CH_3CONHCIC_6H_5^+$ is not the substance undergoing transformation into parachloracetanilide, but that

the undissociated salt $\text{CH}_3\text{CONHCl}_2\text{C}_6\text{H}_5$ changes into parachloracetanilide and hydrochloric acid.

What is the evidence supporting the view that such a substance, present in only a very small amount at any moment, can change rapidly enough to account for the reaction velocity?

Jackson and Clarke¹ and also Fries² have shown that $(\text{CH}_3)_3\text{NBr}_2\text{C}_6\text{H}_5$ and other similar substances, which are entirely analogous to the above salt, rearrange very rapidly into parabromdimethylaniline hydrobromide.

The following evidence leaves no doubt that the above is the correct interpretation of the reaction. If the acetylhalogenaminobenzene adds the halogen acid as illustrated above, we should obtain the same intermediate product from acetylchloraminobenzene and hydrobromic acid as is formed by the action of hydrochloric acid on acetylbromaminobenzene:



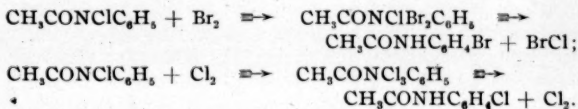
If this addition product is the substance which rearranges into the parahalogenacetanilide, we should obtain the same substance or substances by either of these methods, and the relative amount of parachloracetanilide and parabromacetanilide formed would depend upon the relative tendency of the chlorine and bromine to enter the benzene nucleus. It was known beforehand that acetylbromaminobenzene rearranges very much more rapidly into parabromacetanilide than the corresponding chlor derivative yields parachloracetanilide; we therefore predicted that from both of the reactions we should obtain the same product, parabromacetanilide, and this was happily verified by experiment. The parabromacetanilide obtained seemed to be practically free from parachloracetanilide. The formation of the parabromacetanilide from acetylchloraminobenzene and hydrobromic acid takes

¹ THIS JOURNAL, 34, 261; 36, 409.

² Ann. Chem. (Liebig), 346, 128.

place according to a reaction of the second order as demanded by equation (A) above.

We have further found that when bromine or chlorine is added to acetylchloraminobenzene in ligroin the substance is transformed in a few seconds into parabromacetanilide and parachloracetanilide. The formation of the parabromacetanilide was predicted.



The transformation of these acetylhalogenaminobenzenes in the presence of acids was effected in aqueous acetic acid solutions. If the cation in (1) were the substance being transformed into parahalogenacetanilide this rearrangement should take place more rapidly in those solutions containing more water, because in such solutions the salt would be more completely dissociated. But if the undissociated salt in (5) is the substance being changed into the halogenacetanilide the rearrangement should take place more slowly in those solutions containing more water, because there would be less undissociated salt in the solutions containing more water. Since the concentration of the undissociated salt would be smaller the velocity of transformation of the acetylhalogenaminobenzene would be smaller. Since the rearrangements take place more slowly in those solutions containing more water, the latter hypothesis and equations (5) and (6) are verified.

Finally, if the undissociated salt were the substance being transformed the addition of a salt with a common ion should cause a rise in the velocity of transformation. It is evident that the addition of potassium chloride to a solution of the acetylchloraminobenzene and hydrochloric acid would cause a suppression of the ionization of the complex hydrochloride. If the undissociated salt is the substance being transformed it is evident that the increase of the concentration of this substance by the potassium chloride should cause an increase in the reaction velocity. The theory has been fully verified

experimentally as will be shown below. If the complex cation were the substance undergoing transformation the addition of potassium chloride should cause a decrease in the ionization and velocity of reaction, provided that the potassium chloride does not act *per se* as an energetic positive catalyzer. Such is, however, not the case.

It is entirely possible that the rearrangements of derivatives of phenylnitramine, phenylnitrosamine, and phenylsulphaminic acid into derivatives of nitraniline, nitrosoaniline and sulphanilic acid take place like the above reactions, and this will be a subject of investigation in this laboratory.

EXPERIMENTAL.

The acetylchloraminobenzene and the acetylbromaminobenzene used in the following experiments were prepared by Slosson's¹ method, as the methods of Chattaway and Orton² and of Armstrong³ were tried without good results.

Five-tenths gram of acetylchloraminobenzene, melting at 85°-87°, was dissolved in ligroin and 0.25 cc. of bromine were dropped in; a white precipitate of parabromacetanilide was formed immediately. This was filtered off after a few moments, dried and recrystallized from alcohol. It melted at 163°-167°; when mixed with pure parabromacetanilide, m. p. 167°, obtained by another method, the melting-point was not lowered.

One-half gram of acetylchloraminobenzene, m. p. 85°-87°, was dissolved in ligroin and a rapid stream of dry chlorine gas was passed in. After one minute a white precipitate of parachloracetanilide began to appear. When the precipitation was complete, the substance was filtered off, dried, and recrystallized from alcohol. It melted at 173°-176°. When mixed with parabromacetanilide, m. p. 167°, it melted at 165°-170°. When mixed with pure parachloracetanilide, m. p. 176°-178°, made from acetylchloraminobenzene and hydrochloric acid, it melted at 176°-178°.

Acetylchloraminobenzene, m. p. 85°-87°, was dissolved

¹ *Loc. cit.*

² *Ibid.*

³ *Ibid.*

in glacial acetic acid and treated with dilute hydrochloric acid. A white precipitate of parachloroacetanilide was obtained which, when crystallized from alcohol, melted at 176° – 178° .

Acetylchloraminobenzene, m. p. 85° – 87° , was dissolved in glacial acetic acid and treated with dilute hydrobromic acid. A white precipitate of parabromacetanilide was obtained which melted at 165° – 167° when crystallized from alcohol. When mixed with parabromacetanilide, m. p. 167° , obtained from acetylbromaminobenzene and hydrobromic acid the melting-point was still 165° – 167° . When mixed with pure parachloroacetanilide, m. p. 176° – 178° , the melting-point was lowered to 150° – 160° .

One gram of acetylchloraminobenzene, m. p. 85° – 87° , was treated with a large excess of dilute sulphuric acid and let stand two weeks. The product was filtered off and recrystallized from alcohol. It then melted at 88° – 89° . A sample of 0.2927 gram required 28.80 cc. of 0.1185 N sodium thiosulphate solution. The substance then was unchanged acetylchloraminobenzene, 99 per cent pure. This experiment shows that sulphuric acid causes only a very slow change in the substance. Quantitative experiments given below show further that this change is very slow when the acetylchloraminobenzene and sulphuric acid are dissolved in aqueous acetic acid. The experiment proves very clearly that the catalysis is not due to the mere presence of the hydrogen ions, because the rapidity of rearrangement caused by the sulphuric acid in a given concentration is very much less than that produced by an equal concentration of hydrochloric acid or hydrobromic acid.

Acetylbromaminobenzene, m. p. 88° , was treated with dilute hydrochloric acid. A white precipitate of parabromacetanilide was obtained which, when recrystallized from alcohol, melted at 167° , and this melting-point was not lowered by mixing the sample with parabromacetanilide obtained otherwise.

Acetylbromaminobenzene, m. p. 88° , was treated with dilute hydrobromic acid. A precipitate of parabromacetanilide was obtained which, when recrystallized from alcohol,

melted at 167°. The melting-point was not lowered by mixing the sample with the above compound, or with pure parabromacetanilide obtained otherwise.

Paratolylacetylnitrogenbromide, prepared by Chattaway and Orton's method, rearranged so quickly on standing, or when treated with hydrochloric or hydrobromic acid, that it was impossible to do any quantitative work with this substance.

The paratolylacetylnitrogenchloride used in the rearrangement experiments was prepared by Chattaway and Orton's method. This substance, when treated with hydrochloric acid, gave a mixture of paracetoluidide and orthochloroparacetoluidide.

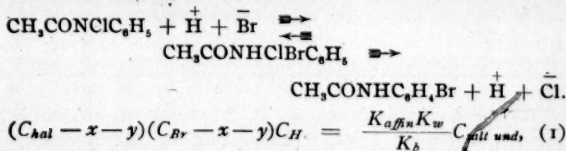
Paratolylacetylnitrogenchloride, when treated with a large excess of hydrobromic acid, gave a red oil from which a compound was obtained by recrystallization from alcohol. This melted at 107°–108° and was probably impure orthobromoparacetoluidide, m. p. 118°.

Paratolylacetylnitrogenchloride, in ligroin solution, was decomposed by bromine and chlorine, giving, in both cases, apparently some impure paracetoluidide, melting at 140°–150°.

REARRANGEMENT EXPERIMENTS.

Experiments with Hydrobromic Acid.

If in the reaction between hydrobromic acid and acetylchloraminobenzene the parabromacetanilide is formed by the rearrangement of the undissociated hydrobromide of the acetylchloraminobenzene, the equations will differ somewhat in form from those used in the work on the rearrangements produced by hydrochloric acid. If the undissociated salt is formed according to the mass law we have



or, when y is small in comparison with x ,

$$(C_{hal} - x)(C_{Br} - x)C_H = \frac{K_{affn} K_w}{K_b} C_{salt\ und}, \quad (2)$$

in which y is the concentration of the salt formed, and x the concentration of the parabromacetanilide, while the other symbols have the same meaning as before.

If now the undissociated salt is the substance undergoing rearrangement, we have

$$-\frac{dC_{salt\ und}}{dt} = K_{trans} C_{salt\ und}. \quad (3)$$

As discussed above, however, we can substitute for $C_{salt\ und}$ in (3) the corresponding value in (2) and we then get

$$\frac{dx}{dt} = \frac{K_{trans} K_b}{K_{affn} K_w} (C_{hal} - x)(C_{Br} - x)C_H = K(C_{hal} - x)(C_{Br} - x)C_H. \quad (4)$$

When C_{hal} , C_{Br} and C_H are in equivalent concentrations, A , equation (4) becomes

$$\frac{dx}{dt} = K(A - x)(A - x)A \quad \text{or} \quad \frac{x}{t(A - x)A} = K, \quad (5)$$

whereas if only the concentrations of the acetylchloraminobenzene and of the bromide ions were to be considered the well-known equation by the second order reaction,

$$\frac{x}{t(A - x)A} = K,$$

would hold. We have therefore a method of testing the question whether the undissociated salt formed by the union of the hydrobromic acid with the acetylchloraminobenzene is the substance rearranging according to equation (5). By simply varying the value of A , we can see if a constant value for K is obtained. We must, however, expect some decrease in the value of K with increase in the value of A for the following reasons: The A in equation (5) is substituted for $(C_{hal} - y)$ or $(C_{Br} - y)$ in equation (1). When y is very small the error involved in this substitution is small. Since y increases more rapidly than A it is evident that the error becomes

larger with increase in A , and since A^2 occurs in the denominator in equation (5) the error is still more magnified. Instead of A^2 in equation (5) we should have $(A-y)^2$, the value of which is not known. Since then A^2 is larger than $(A-y)^2$ and occurs in the denominator the value of K should decrease with increase in the value of A .

Since A^2 is the function used in equation (5), even a small error involved in the use of A instead of $(A-y)$ becomes magnified in A^2 . If $(A-y)$ equals 0.9 A , the value of K derived from equation (5) is 20 per cent less than it should be, whereas if $(A-y)$ equals 0.6 A the value of K is only one-third as large as it should be. This fact then accounts to some extent for the decrease in the value of K in Tables I. and IX. inclusive. The results of all the work on the rearrangements by hydrochloric acid and hydrobromic acid makes it very probable that the above explanation of the cause of the rearrangement is essentially correct. It is probable, however, that there are other conditions not considered at all in the above equations which help to cause a decrease in the value of K in Tables I. to IX., inclusive, and these are now the subject of investigation.

The experiments in Tables I. to IX. were carried out in the following manner in a dark room. From 0.2 gram to 2.2 grams acetylchloraminobenzene were put into a dark colored bottle holding something more than 600 cc. The solid was then dissolved in 60 cc. glacial acetic acid and afterwards 540 cc. water were added. The contents of the bottle were shaken up thoroughly and placed in a bath of melting ice. When the temperature had become constant, 100 cc. were withdrawn in a pipette and quickly transferred to a beaker containing 1.0-2.0 grams of potassium iodide in 10-20 cc. of water. The iodine liberated by the unchanged acetylhalogenaminobenzene derivative was titrated with standard sodium thiosulphate. From this it was possible to calculate the necessary amount of standard hydrobromic acid to be added to the remaining 500 cc. of solution to make unimolecular equivalents. The time was noted when this acid was added; 100 cc. were withdrawn in a pipette from time to time, added to the potassium

iodide solution, and the iodine titrated against sodium thiosulphate solution as above. The results gave no constant at all for a monomolecular equation, but a very fair one for the bimolecular equation. The time, T , is expressed in minutes in all of the following tables. In calculating the results the necessary correction for the change in volume by the addition of the acid was made. The hydrochloric acid liberated during the reaction acts so slowly, in comparison with the hydrobromic acid, upon the acetylchloraminobenzene that this factor is not considered in the above equations.

In Tables I. to IX. inclusive the value K is calculated from AK on the basis of number of cc. thiosulphate solution used. K' is calculated from AK on the basis of the number of gram molecules per liter of acetylchloraminobenzene.

In Tables X. to XIV. inclusive, approximately 2.0 grams of acetylchloraminobenzene derivative were dissolved in the same volume of solvent used above. In these tables the value of K is calculated from that of AK on the basis that the quantity of acetylchloraminobenzene derivative present is equivalent to 20 cc. thiosulphate solution. The values 0.255, 0.260, and 0.275 of K for acetylchloraminobenzene at 2°, 4° and 5° agree very closely.

Table I.

0.2 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3°; 1.16 cc. of 1.05 N HBr (1 mol.) added.

t	$\text{Na}_2\text{S}_2\text{O}_3$	$A^{\circ}K$
0	5.31	
21.66	4.32	0.0106
46.16	3.54	0.0108
78.16	2.82	0.0113
114.5	2.28	0.0116
157.16	1.90	0.0114

Average, 0.0111

K , 0.00039

K' , 0.13

Table II.

0.4 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3°; 1.91 cc. of 1.05 N HBr (1 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	A°K.
0	8.69	
1.0	8.53	0.0188
3.66	8.10	0.0199
16.0	6.45	0.0217
40.66	4.58	0.0220
95.33	2.70	0.0232

Average, 0.0211

K, 0.00028

K', 0.095

Table III.

0.6 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3°; 2.79 cc. of 1.05 N HBr (1 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	KA°.
0	12.69	
11.25	8.92	0.0376
18.66	7.40	0.0382
36.33	5.23	0.0392
54.5	4.02	0.0395
76.25	3.16	0.0395

Average, 0.0388

K, 0.00024

K', 0.081

Table IV.

0.8 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3°; 3.72 cc. of 1.05 N HBr (1 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	KA°.
0	16.88	
3.08	14.41	0.0556
8.16	11.55	0.0565
16.66	8.70	0.0564
34.33	5.73	0.0566
62.8	3.60	0.0587

Average, 0.0568

K, 0.00019

K', 0.067

Table V.

1.1 grams acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3°; 5.18 cc. of 1.094 N HBr (1 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	KA^3
0	24.43	
3	18.90	0.0975
11.66	11.37	0.0984
20.25	8.06	0.100
44.5	4.25	0.106
128.5	1.32	(0.136)

Average, 0.100

K , 0.00017

K' , 0.055

Table VI.

1.6 grams acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3°; 7.84 cc. of 1.094 N HBr (1 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	KA^3
0	36.78	
1.08	30.10	0.205
3.08	22.00	0.218
10	12.73	0.189
23.5	6.39	0.202
41.16	3.80	0.210

Average, 0.205

K , 0.00015

K' , 0.051

Table VII.

2.2 grams acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3°; 10.52 cc. of 1.094 N HBr (1 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	KA^3
0	49.12	
0.92	36.46	(0.378)
2.58	26.22	0.338
4.66	18.79	0.347
11.16	9.96	0.352
21.66	5.80	0.344

Average, 0.345

K , 0.00014

K' , 0.048

Table VIII.

1.0 gram acetylchloraminobenzene (3 mols.) in 60 cc. glacial acetic acid and 540 cc. water at 3°; 1.52 cc. of 1.094 N HBr (1 mol.) added.

t	$\text{Na}_2\text{S}_2\text{O}_3$	$\frac{1}{t} \log \frac{B(A-x)}{A(B-x)} = K(A-B)B.$
0	21.62	
1	18.80	0.015
30	16.27	0.015
60	14.82	0.015
150	13.93	
361	13.94	
1440	13.32	
		Average, 0.015

K , 0.00014

Table IX.

0.333 gram acetylchloraminobenzene (1 mol.) in 60 cc. glacial acetic acid and 540 cc. water at 3°; 4.53 cc. of 1.094 N HBr (3 mols.) added.

t	$\text{Na}_2\text{S}_2\text{O}_3$	$\frac{1}{t} \log \frac{B(A-x)}{A(B-x)} = K(A-B)B.$
0	7.14	
2.16	6.21	(0.029)
6.25	4.65	0.021
14	2.82	0.022
27.75	1.26	0.021
59	0.20	
202	0.00	

Average, 0.021

K , 0.00021

Table X.

0.8 gram acetylchloraminobenzene in 30 cc. glacial acetic acid and 265 cc. water at 2°; 3.81 cc. (1 mol.) of 1.05 N HBr added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	A.K.
0	17.31	
1.0	14.01	0.236
3.75	9.87	0.196
14.75	4.37	0.203
25.25	2.37	0.252
48.50	1.56	0.208

Average, 0.22

K, 0.255

Table XI.

0.8 gram acetylchloraminobenzene in 30 cc. glacial acetic acid and 2.70 cc. water at 4°; 4.61 cc. of 1.05 N HBr (1 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	A.K.
0	20.60	
1.12	16.57	0.216
2.87	11.56	0.272
7.63	6.44	0.288
15.50	3.30	0.329
33.75	2.18	0.250

Average, 0.27

K, 0.26

Table XII.

0.8 gram acetylchloraminobenzene in 30 cc. glacial acetic acid and 278 cc. water at 5°; 4.39 cc. of 1.05 N HBr (1 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	A.K.
0	19.62	
0.87	15.10	(0.34)
3.25	10.28	0.28
8.37	6.01	0.27
16.00	3.72	0.27
32.00	2.18	0.25

Average, 0.27

K, 0.275

The reaction between hydrobromic acid and paratolylacetylnitrogenchloride was studied and the results are given in the following tables. Conditions were the same as with the acetylchloraminobenzene. In each case the constant was calculated from the bimolecular equation. The two sets of constants agree very well and show the rearrangement of the paratolylacetylnitrogenchloride by one molecular quantity of hydrobromic acid to be only about one-third as rapid as that of the acetylchloraminobenzene.

Table XIII.

0.7 gram paratolylacetylnitrogenchloride in 30 cc. glacial acetic acid and 270 cc. water at 5°; 2.65 cc. of 1.05 N HBr (1 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	AK.
0	11.94	
3.00	10.15	0.059
8.25	8.02	0.059
18.50	5.77	0.058
36.50	4.38	(0.047)
		Average, 0.058

K, 0.098

Table XIV.

0.7 gram paratolylacetylnitrogenchloride in 30 cc. glacial acetic acid and 270 cc. water at 5°; 2.69 cc. of 1.055 N HBr (1 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	AK.
0	12.09	
1.50	11.06	0.062
5.00	9.37	0.058
18.00	5.89	0.058
30.00	4.47	0.057
50.00	3.30	0.053
		Average, 0.058

K, 0.098

Rearrangement Experiments with Hydrochloric Acid.

The constant in each case is calculated from the monomolecular equation (6) $\frac{1}{t} \log \frac{A}{A-x} = KC_H^2$. In the following series of experiments with acetylchloraminobenzene and hydrochloric acid, the acid was added in amounts equivalent to those of Blanksma¹ when he used 10, 15, 20, etc., cc. of 28.67 per cent hydrochloric acid to 500 cc. of solution. We used the same proportion of a different strength of acid to 250 cc. of solution. Ten cc. of 28.67 per cent hydrochloric acid to 500 cc. solution are taken as the standard and will be designated as *M* amount of acid; others will be 2*M*, 3*M*, etc. Corrections were applied for the difference in volume when the acid was added to the standard solution of the acetylchloraminobenzene derivative instead of making the entire solution standard as Blanksma did. Tables XV. to XVIII., inclusive, show that the velocity constant decreases with increasing per cent of water.

Tables XIX. and XX. show the relative reaction velocities at 4° and 25°.

Tables XXI. to XXVII., inclusive, show the change of velocity of transformation with change in concentration of hydrochloric acid in 20 per cent acetic acid solution at 25°.

Tables XXVIII. to XXXIV., inclusive, show the change of velocity of transformation with change in concentration of hydrochloric acid in 30 per cent acetic acid solution at 25°.

Tables XXXV. and XXXVI. are a general resumé of Tables XXI. to XXXIV., inclusive, and of Blanksma's work, showing that the velocity of the transformation increases as the square of the concentration of the hydrochloric acid. The change in percentage of ionization of the hydrochloric acid with the small changes in dilution used in these experiments is small and hardly affects the values of the constant.

Tables XXXVII. to XLIII., inclusive, are a miscellaneous set showing the velocity of transformation of acetylchloraminobenzene by sulphuric acid and by acetic acid, and the velocity of transformation of paratolylacetyl nitrobenzyl chloride by hydrochloric acid.

¹ *Loc. cit.*

The investigation will be continued.

Table XV.

2.0 grams acetylchloraminobenzene in 180 cc. glacial acetic acid and 120 cc. water at 25°; 8.58 cc. of 5.49 N HCl (1.2 mol.) added.

<i>t</i> .	$\text{Na}_2\text{S}_2\text{O}_3$.	K.
0	43.19	
5	27.32	0.029
10	16.32	0.031
15	9.43	0.033
20	5.56	0.033
30	2.02	0.033

Average, 0.032

Table XVI.

1.0 gram acetylchloraminobenzene dissolved in 120 cc. glacial acetic acid and 180 cc. water at 25°; 7.16 cc. of 5.49 N HCl (1 mol.) added.

<i>t</i> .	$\text{Na}_2\text{S}_2\text{O}_3$.	K.
0	18.65	
15	15.38	0.0057
30	12.68	0.0057
60	8.84	0.0057
75	7.24	0.0055
95	5.82	0.0055
120	4.32	0.0054
160	2.62	0.0054

Average, 0.0055

Table XVII.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 210 cc. water at 25°; 7.16 cc. of 5.49 N HCl (1 mol.) added.

<i>t</i> .	$\text{Na}_2\text{S}_2\text{O}_3$.	K.
0	18.68	
60	11.00	0.0038
95	8.25	0.0037
120	6.83	0.0036
150	5.37	0.0036
180	4.46	0.0035

Average, 0.0036

Table XVIII.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 240 cc. water at 25°; 7.16 cc. of 5.49 N HCl (1 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	<i>K.</i>
0	17.92	
63	12.63	0.0024
120	9.50	0.0023
180	7.21	0.0022
240	5.63	0.0021
300	4.48	0.0020

Average, 0.0022

The two following tables are given to show the temperature coefficient for the reaction at 4° and at 25°. The velocity of transformation is about 3.5 times as great at 25° as at 4°.

Table XIX.

1.10 grams acetylchloraminobenzene in 30 cc. glacial acetic acid and 270 cc. water at 4°; 1.5 cc. of 6.59 N HCl added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	<i>K.</i>
0	15.60	
61	15.38	(0.00010)
232	15.29	0.000038
482	15.02	0.000035
1140	14.50	0.000027
1663	14.06	0.000027

Average, 0.000032

Table XX.

1.0 gram acetylchloraminobenzene in 30 cc. glacial acetic acid and 270 cc. water at 25°; 1.5 cc. of 6.59 N HCl added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	<i>K.</i>
0	16.17	
120	15.62	0.00012
270	15.01	0.00012
438	14.34	0.00012
600	13.94	0.00011
1280	13.01	0.00007
1783	10.62	0.00010

Average, 0.00011

The following sets of tables show the variation in the velocity constants with variations in the concentration of the hydrochloric acid when the concentration of the acetylchloraminobenzene is approximately the same in all the experiments.

Table XXI.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 237.44 cc. water at 25°; 2.56 cc. of 7.68 N HCl (0.5 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	K.
0	13.44	
60	12.30	0.00064
150	10.72	0.00065
240	9.27	0.00067
390	7.44	0.00066
580	6.10	0.00060
Average,		0.00064

Table XXII.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 240 cc. water at 25°; 7.16 cc. of 5.49 N HCl (1 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	K.
0	17.92	
63	12.63	0.0024
120	9.50	0.0023
180	7.21	0.0022
240	5.63	0.0021
300	4.48	0.0020
Average,		0.0022

Table XXIII.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 240 cc. water at 25°; 10.74 cc. of 5.49 N HCl (1.5 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	<i>K.</i>
0	22.12	
30	17.31	(0.0036)
60	12.34	0.0042
90	9.17	0.0043
120	6.88	0.0042
150	5.24	0.0041
180	4.14	0.0041

Average, 0.0041

Table XXIV.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 240 cc. water at 25°; 14.49 cc. of 5.45 N HCl (2 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	<i>K.</i>
0	21.05	
30	13.66	0.0067
45	10.78	0.0068
60	8.39	0.0071
75	6.62	0.0072
90	5.34	0.0068

Average, 0.0069

Table XXV.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 221.86 cc. water at 25°; 18.16 cc. of 5.45 N HCl (2.5 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	<i>K.</i>
0	22.26	
10	16.38	0.0133
20	12.30	0.0126
30	9.14	0.0129
40	6.94	0.0127
50	5.30	0.0125

Average, 0.0128

Table XXVI.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 218.2 cc. water at 25°; 21.80 cc. of 5.45 N HCl (3 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	K.
0	22.52	
5	17.81	0.0204
10	14.08	0.0204
15	11.23	0.0202
25	7.16	0.0199
40	3.74	0.0195

Average, 0.0201

Table XXVII.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 213.4 cc. water at 25°; 26.6 cc. of 7.68 N HCl (5 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	K.
0	16.13	
3	9.96	0.0698
6	6.36	0.0674
9	3.93	0.0681
15	1.68	0.0655
21	1.82	0.0616

Average, 0.0663

Table XXVIII.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 207.44 cc. water at 25°; 2.56 cc. of 7.68 N HCl (0.5 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	K.
0	15.20	
60	12.22	(0.0016)
120	11.49	0.00101
210	9.25	0.00102
330	6.92	0.00103
480	4.76	0.00105

Average, 0.00103

Table XXIX.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 210 cc. water at 25°; 7.16 cc. of 5.49 N HCl (1 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	<i>K.</i>
0	18.68	
60	11.00	0.0038
95	8.25	0.0037
120	6.83	0.0036
150	5.37	0.0036
180	4.46	0.0035

Average, 0.0036

Table XXX.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 202.32 cc. water at 25°; 7.68 cc. of 7.68 N HCl (1.5 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	<i>K.</i>
0	18.15	
15	13.42	0.0087
30	9.99	0.0086
45	7.42	0.0087
60	5.52	0.0086
75	4.18	0.0085

Average, 0.0086

Table XXXI.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 195.47 cc. water at 25°; 14.53 cc. of 5.45 N HCl (2 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	<i>K.</i>
0	22.72	
10	16.23	0.0146
20	11.57	0.0147
30	8.22	0.0147
55	3.61	0.0145
80	1.73	0.0148

Average, 0.0146

Table XXXII.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 197.2 cc. water at 25°; 12.80 cc. of 7.68 N HCl (2.5 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	K.
0	17.10	
5	13.02	0.0277
10	9.97	0.0234
15	7.72	0.0230
20	5.90	0.0231
30	3.60	0.0226

Average, 0.024

Table XXXIII.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 194.64 cc. water at 25°; 15.36 cc. of 7.68 N HCl (3 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	K.
0	17.19	
3	13.90	0.0307
7	10.34	0.0315
11	7.78	0.0313
15	5.80	0.0315
19	4.32	0.0316

Average, 0.0313

Table XXXIV.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 184.4 cc. water at 25°; 25.6 cc. of 7.68 N HCl (5 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_3$	K.
0	17.95	
2	10.42	0.118
4	6.16	0.116
6	3.73	0.114
8	2.29	0.112
12	0.92	0.108

Average, 0.114

Summary.

The two following tables give a summary of the preceding ones and of Blanksma's work. Ordinary logarithms were used instead of the natural system. The list under "glacial acetic acid" gives the volume per cent of acetic acid used in the solution. The table under HCl gives the concentrations of the hydrochloric acid, calculated as explained above. The constants in parenthesis are the values calculated from the average constant. It will be noticed that the agreement between the calculated and found values is very good. Blanksma's table shows that an increase of 10 per cent in the concentration of the acetic acid causes approximately a doubling of the constants.

Table XXXV.

	HCl.					
	0.5 M.	1 M.	1.5 M.	2 M.	2.5 M.	3 M.
Glacial acetic acid.						
20 per cent	0.00065 (0.00056)	0.0022 (0.0021)	0.0041 (0.0048)	0.0070 (0.0086)	0.0128 (0.0133)	0.0201 (0.0199)
30 per cent	0.00103 (0.00098)	0.0036 (0.0039)	0.0087 (0.0087)	0.0146 (0.0154)	0.0239 (0.0242)	0.0313 (0.0348)
40 per cent		0.0556				
60 per cent		0.033				

Table XXXVI. (Blanksma's).

		HCl.			
Glacial acetic acid.		10 cc.	15 cc.	20 cc.	25 cc.
20 per cent		0.00218	0.00419	0.00814	0.0104
30 "		0.00364	0.00802	0.0137	0.0198
40 "		0.00676	0.0144	0.0253	
50 "		0.0155	0.0309		
60 "		0.036			

Table XXXVII.

The effect of the suppression of ionization was studied. 1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 227.2 cc. water at 25°; 4.4 grams of KCl (10 mol.) and 12.80 cc. of 7.68 N HCl (2.5 mol.) added. The effect was to increase greatly the velocity of reaction.

t.	Na ₂ S ₂ O ₃ .	K.
0	16.83	
10	10.84	0.0191
20	6.88	0.0194
30	4.50	0.0191
40	2.92	0.0190
50	1.84	0.0192
		Average, 0.0192

Table XXXVIII.

KCl alone causes very little change. 1 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 240 cc. water at 25°; 4.4 grams KCl (10 mol.) added.

t.	Na ₂ S ₂ O ₃ .	K.
0	16.02	
30	15.74	(0.00025)
90	15.64	0.00012
185	15.08	0.00014
300	14.65	0.00013
420	14.00	0.00014
		Average, 0.00013

Table XXXIX.

Glacial acetic acid alone causes very little rearrangement; 1 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 210 cc. water at 25°.

t.	$\text{Na}_2\text{S}_2\text{O}_3$.	K.
0	16.70	
120	16.63	0.000015
360	16.54	0.000012
1380	16.45	0.0000048
1900	16.41	0.0000040
2935	16.37	0.0000029

Table XL.

Rearrangement experiment with sulphuric acid; 1.1 grams acetylchloraminobenzene in 30 cc. glacial acetic acid and 270 cc. water at 4°; 5.3 cc. of $\text{N H}_2\text{SO}_4$ added.

t.	$\text{Na}_2\text{S}_2\text{O}_3$.	K.
0	21.37	
4	20.82	0.0028
36	20.75	0.00036
103	19.93	0.00029
969	17.01	0.00010
4115	15.88	0.000031
8190	13.26	0.000025

Table XLI.

0.7 gram paratolylacetylnitrogenchloride in 30 cc. glacial acetic acid and 270 cc. water at 3°; 2.50 cc. of 6.59 N HCl (5 mol.) added.

t.	$\text{Na}_2\text{S}_2\text{O}_3$.	K.
0	14.19	
28.12	13.63	0.00062
58.50	13.10	0.00059
120.75	12.18	0.00055
289.87	9.47	0.00061
420.00	7.56	0.00065

Average, 0.00061

Table XLII.

0.7 gram paratolylacetylnitrogenchloride in 30 cc. glacial acetic acid and 260 cc. water at 3.5°; 7.82 cc. of 6.59 N HCl (20 mol.) added.

<i>t</i>	Na ₂ S ₂ O ₃	K.
0	11.25	
16.5	11.05	(0.00092)
45	10.96	0.00025
90	10.67	0.00025
150	10.19	0.00028
300	7.96	0.00030
Average,		0.00027

Table XLIII.

0.6 gram paratolylacetylnitrogenchloride in 30 cc. glacial acetic acid and 260 cc. water at 3°; 7.82 cc. of 5.49 N HCl (20 mol.) added.

<i>t</i>	Na ₂ S ₂ O ₃	K.
0	9.32	
30	9.05	(0.00043)
60	8.98	0.00027
90	8.80	0.00028
150	8.42	0.00029
360	7.14	0.00032
Average,		0.00029

While Tables XLII. and XLIII. agree very well, they do not harmonize with Table XLI. and the general results obtained above. In Tables XLI., XLII. and XLIII. the concentration of the hydrochloric acid used was calculated from the concentration of the paratolylacetylnitrogenchloride.

GENERAL DISCUSSION OF THE HYDROLYSIS OF AMIDES, CANE-SUGAR, OXIMES AND ESTERS.

In the hydrolysis of esters, cane-sugar, amides, amidines, nitriles, oximes and related compounds we are dealing with weak bases in the presence of acids and water. Many salts of these weak bases, amides, nitriles, esters and oximes, have been isolated and studied. The affinity constant for acet-

amide,¹ for instance, is 3×10^{-15} at 25° , and that for propionitrile at the same temperature is 1.8×10^{-15} . The work of Collie and Tickle,² Baeyer and Villiger,³ Werner,⁴ Brühl,⁵ Archibald and McIntosh,⁶ Walden,⁷ van't Hoff⁸ and many others leaves no doubt that esters, ketones, alcohols, sugars, ethers, and organic acids are weak bases and form tetravalent oxygen salts which are derivatives of the hypothetical oxonium hydroxide, H_2OOH . The work of Sackur,⁹ Kablukoff,¹⁰ Coehn,¹¹ Walden,¹² Baeyer and Villiger, Collie and Tickle, Archibald and McIntosh and Walker¹³ have shown conclusively that these salts are electrolytes, in which the tetravalent oxygen compound probably forms part of the cathion. The affinity constant of dimethylpyrone as a base, for instance, was found to be about 2.4×10^{-14} . In cane-sugar, ethers, and similar compounds we have a COC linkage, which can

H
|
form salts, COC . There is plenty of evidence to show that

Cl

all these compounds have both basic and acid properties.

Now the work of Arrhenius,¹⁴ of Walker¹⁵ and of Shields¹⁶ has shown that when these weak bases are treated with acids a small amount of salt is formed according to the following equation:

$$(C_{sub} - x) \times C_H = K_{hyd} C_{salt} dls = \frac{K_w}{K_b} C_{salt} dls, \quad (1)$$

¹ Z. physik. Chem., **4**, 319. Ahren's Sammlung, Abegg, **8**, 183.

² J. Chem. Soc., **78**, 710.

³ Ber. d. chem. Ges., **34**, 2692; **35**, 1201.

⁴ Ann. Chem. (Liebig), **333**, 296. Ber. d. chem. Ges., **34**, 3300.

⁵ *Ibid.*, **38**, 2847, 2866. Z. physik. Chem., **18**, 514.

⁶ *Ibid.*, **55**, 129. Phil. Trans., **205**, 99. J. Chem. Soc., **85**, 919.

⁷ Ber. d. chem. Ges., **34**, 4185.

⁸ Ansichten über die Organische Chemie, I Theil, p. 62, fol.

⁹ Ber. d. chem. Ges., **35**, 1242.

¹⁰ Z. physik. Chem., **4**, 429.

¹¹ Ber. d. chem. Ges., **35**, 2673.

¹² *Ibid.*, **34**, 4185; **35**, 1764.

¹³ J. Chem. Soc., **85**, 1098. Ber. d. chem. Ges., **34**, 4115.

¹⁴ Z. physik. Chem., **5**, 1; **13**, 407.

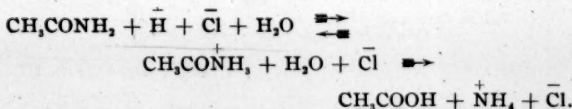
¹⁵ *Ibid.*, **4**, 319; **23**, 137; J. Chem. Soc., **77**, 5.

¹⁶ Z. physik. Chem., **13**, 167.

in which, C_{sub} is the original concentration of the base in gram molecules per liter, x the amount of base transformed into the other products at any moment, $(C_{sub} - x)$ the concentration of the base at any moment, C_H that of the hydrogen ions, $C_{salt\ dis}$ that of the dissociated portion of the salt, practically all ionized, K_{hyd} the hydrolysis constant, K_b the affinity constant of the base and K_w the ion product for water at the given temperature. But the amount of salt, $C_{salt\ dis}$, present in such cases is extremely small and for $(C_{sub} - x)$ and C_H we may substitute, without appreciable error, the values they would have if no salt were formed. In those cases in which $C_{salt\ dis}$ is large this cannot be done, but the concentrations of each substance can be determined from (1).

It is the opinion of a large number of chemists that the above salts are intermediate compounds in the catalytic transformations spoken of, and that such catalytic reactions are brought about solely because of, and through, the formation of such intermediate compounds.

The work of Remsen and Reid¹ on the hydrolysis of amides by acids, and of Acree and Johnson² from theoretical grounds, indicated an intermediate formation of an amide salt, the cation of which reacts with water and forms an acid and the ammonium ion, just as the urazole ion reacts with the neutral ethyl iodide.

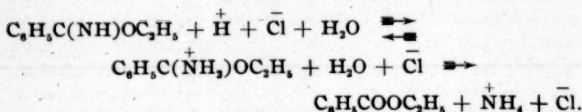


This idea is fully verified by the work of Mr. Sidney Nirdlinger appearing in the succeeding article and by all the data of Ostwald. Julius Stieglitz³ has further verified this by work on the hydrolysis of imido esters in the presence of acids, in that he showed that the imido ester cation is hydrolyzed:

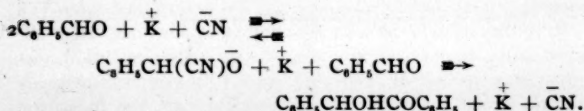
¹ THIS JOURNAL, 21, 281; Reid: *Ibid.*, 24, 397.

² *Ibid.*, 27, 410.

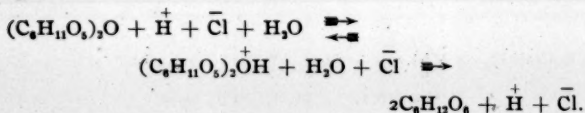
³ Congress of Arts and Science, St. Louis, 1904, 4, 276.



Lapworth¹ and then Bredig and Stern² showed that cyanides act catalytically in causing such condensations as the formation of benzoin from benzaldehyde, solely because the cyanide ion unites with benzaldehyde and forms a complex anion which reacts with benzaldehyde and yields benzoin and a cyanide ion.



Bredig³ and Euler⁴ suggested that acids cause the catalytic inversion of cane-sugar in water solutions, and of diazoacetic ester and other esters in water because the hydrogen ions unite with the weak bases, sugar and esters, and form salts which are hydrolyzed by the water.



Luther and Sammet⁵ have shown that the equilibrium between iodic acid, hydriodic acid, iodine and water is between the hydrogen, iodide and iodate ions on the one hand and iodine and water on the other and can be expressed by the equation

¹ J. Chem. Soc., **83**, 995.

² Z. Elek. Chem., **10**, 585.

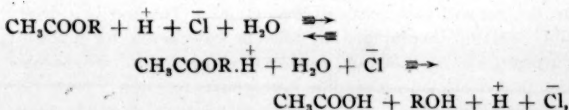
³ *Ibid.*, **9**, 118; **10**, 586; **11**, 528.

⁴ Z. physik. Chem., **86**, 405, 663; **40**, 501; **47**, 356.

⁵ Z. Elek. Chem., **11**, 293.

$$\frac{(\overset{+}{\text{H}})(\overset{-}{\text{IO}_3})(\overset{-}{\text{I}})^5}{(\text{I}_2)^3} = 2.8(\pm 0.3) \times 10^{-47}.$$

Finally, Bredig, Euler,¹ Abegg,² Goldschmidt,³ Wegscheider,⁴ Zengelis,⁵ Lapworth,⁶ Kastle,⁷ Stieglitz,⁸ and Acree and Johnson⁹ have discussed the saponification of esters and formation of esters from the point of view that intermediate ions are the substances transformed. Lapworth, Bredig, Euler, Stieglitz, and Acree and Johnson have believed that an application of the mass law harmonizes with the idea that esters may be saponified by water in the presence of acids because of the intermediate formation of an ester cation which is hydrolyzed,



and Acree and Johnson¹⁰ have shown from theoretical grounds, that the undissociated ester salt is not the substance which chiefly is hydrolyzed.

If now, in the catalysis of cane-sugar, esters, etc., we have, in general, an intermediate salt formation and a direct hydrolysis of complex ion, the velocity of transformation of the cane-sugar must be dependent upon the concentrations of the complex ion and the water, or

$$\frac{-dC_{\text{sub cation}}}{dt} = \frac{dx}{dt} = K_{\text{trans}} C_{\text{sub cation}} \times C_{\text{H}_2\text{O}}, \quad (2)$$

¹ Z. physik. Chem., **36**, 403, 663; **40**, 501; **47**, 356.

² Z. Elek. Chem., **10**, 185.

³ *Ibid.*, **10**, 221.

⁴ Z. physik. Chem., **39**, 257; **41**, 62.

⁵ Ber. d. chem. Ges., **34**, 198.

⁶ See Mellor's "Chemical Statics and Dynamics," 1904, p. 289.

⁷ Private communication. *THIS JOURNAL*, **19**, 894. P. Am. Assn. Adv. Sci., **47**, 238.

⁸ *Loc. cit.*

⁹ *THIS JOURNAL*, **37**, 410.

¹⁰ *Loc. cit.*

in which $-dC_{\text{sub cathion}}$, or dx , is the small amount of $C_{\text{sub cathion}}$ hydrolyzed in the time dt , C_{H_2O} is the original concentration of the water, and x the amount of water which has been used up in the reaction at the time under consideration. The small amount $-dC_{\text{sub cathion}}$ changed in dt is exactly equal in gram equivalents to the small amount dx of sugar and of water changed in the same time interval. We may, therefore, consider these two equivalent in all of the cases under consideration and write dx for the small amount of substance transformed whether it be the intermediate compound or the sugar, ester, etc. The dx represents an increase, whereas $-dC_{\text{sub cathion}}$ represents a decrease; hence the one is the negative of the other.

In the total reaction, expressed by equations (1) and (2), we are dealing with two consecutive reactions. The first is a reversible reaction involving what may be considered, for practical purposes, a bimolecular and a unimolecular reaction. The second is a practically non-reversible bimolecular reaction. Now the concentration of $C_{\text{sub cathion}}$ at any moment depends upon the concentrations of the sugar, hydrogen ions, anions, and water, at the moment and upon the velocities of the first and second reactions. Now the first reaction is the neutralization of a base by an acid, and all such reactions take place, as a rule, immeasurably rapidly. The second reaction is therefore very slow in comparison with the first, and the equilibrium expressed in equation (1) is never appreciably disturbed by the change in the concentration of $C_{\text{sub cathion}}$ in reaction (2).

It is evident then, from (1), that we can substitute

$$\frac{K_b}{K_w}(C_{\text{sub}} - x) \times C_H$$

for $C_{\text{sub cathion}}$ in (2), and we then get

$$\frac{dx}{dt} = K_{\text{trans}} \frac{K_b}{K_w}(C_{\text{sub}} - x) \times C_H \times (C_{H_2O} - x). \quad (3)$$

But this is exactly the relation found experimentally for the hydrolysis of amides, inversion of cane-sugar and the saponification of esters. It is evident, then, that intermediate sugar

cations, ester cations, amide cations, etc., may be the substances chiefly undergoing hydrolysis.

But Acree and Johnson¹ have shown, further, that the undissociated sugar salt, ester salt, or amide salt is certainly not the substance chiefly undergoing hydrolysis.

If such were the case the velocity of transformation of the sugar, ester or amide would be proportional to the concentrations of the undissociated salt and the water, or

$$\frac{-dC_{\text{salt und}}}{dt} = \frac{dx}{dt} = K_{\text{trans}} C_{\text{salt und}} \times (C_{H_2O} - x). \quad (4)$$

But the undissociated salt is in equilibrium with its ions and

$$C_{\text{salt dis}} \times C_{Cl} = K_{\text{affn}} C_{\text{salt und}}. \quad (5)$$

By substituting in (4) the value of $C_{\text{salt und}}$ derived from (1) and (5) under the same conditions discussed above for the sugar cations, we derive

$$\frac{dx}{dt} = \frac{K_{\text{trans}} K_b}{K_{\text{affn}} K_w} (C_{\text{sub}} - x) \times C_H \times C_{Cl} \times (C_{H_2O} - x) = K(C_{\text{sub}} - x) \times C_H^2 \times (C_{H_2O} - x). \quad (6)$$

But equation (6) does not correspond to the facts found experimentally. The velocity of saponification of esters, amides and cane-sugar is not proportional to the *square* of the concentration of the hydrogen ions, but simply to the concentration. Since in a water solution of the weak bases, cane-sugar, esters amides, oximes and acids there are present (1) the free base, that is, the sugar, ester, etc.; (2) the undissociated salt; and (3) the dissociated salt; one of these three must be the substance hydrolyzed. Since the free base, that is, the cane-sugar etc., and the undissociated salt are not chiefly concerned in the hydrolysis, it is evident that the substance undergoing hydrolysis must be the complex cation formed by the union of hydrogen ions with cane-sugar, esters amides, oximes, etc. The equations worked out above are not exact, but the errors involved in using them are probably within the limits of experiment. An exact application of the mass law would lead

¹ *Loc. cit.*

to very complex equations which would hardly lend themselves to a practical solution of the problem with the data now at hand.

We are now in a position to discuss the evidence bearing on each of the above catalytic reactions.

ON THE INVERSION OF CANE-SUGAR IN AQUEOUS SOLUTIONS OF ACIDS.

Ostwald,¹ Cohen,² Smith,³ Wilhelmy,⁴ Arrhenius,⁵ Uhrech,⁶ Spohr⁷ and Trevor⁸ have shown that aqueous solutions of cane-sugar are hardly affected by pure water, but inversion of the sugar takes place upon the addition of acids, although the acid is not used up in the reaction.

The velocity of inversion by acids, or by water, is almost exactly proportional, in dilute solutions, to the concentration of the hydrogen ions, and is expressed by the equation

$$\frac{dx}{dt} = K(C_{\text{sugar}} - x) \times (C_{H_2O} - x) \times C_H. \quad (1)$$

In dilute solutions, since C_H and $(C_{H_2O} - x)$ are approximately constant the reaction is, apparently, one of the first order. In more concentrated solutions, since the factor $(C_{H_2O} - x)$ changes appreciably in value, the reaction proves to be one of the second order. Now cane-sugar has the same "ether" linkage, COC, common to a large number of oxygen compounds which have been shown to have basic properties, and it might be expected to form tetravalent oxygen salts of the same general type, $R_2O.HCl$.

Unfortunately, cane-sugar is not soluble in the solvents from which we could expect to precipitate its hydrochloride. But Hantzsch⁹ has shown that cane-sugar, just as dimethyl-

¹ J. prakt. Chem. [2], **29**, 385; [2], **31**, 307.

² Z. physik. Chem., **28**, 145.

³ *Ibid.*, **28**, 144, 193.

⁴ Pogg. Ann., **81**, 413, 499.

⁵ Z. physik. Chem., **4**, 226.

⁶ Ber. d. chem. Ges., **13**, 1696; **15**, 2130, 2457, 2687; **16**, 762; **17**, 47, 495, 2165; **18**, 3047; **20**, 1836; **23**, 318.

⁷ J. prakt. Chem. [2], **32**, 32; [2], **33**, 265.

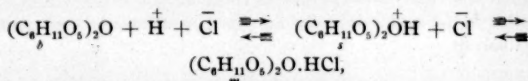
⁸ Z. physik. Chem., **10**, 321.

⁹ Ber. d. chem. Ges., **38**, 2143.

pyrone, glucose and other weak bases, lowers to a small extent the conductivity of sulphuric and hydrochloric acid solutions. Dulcite¹ forms a hydrochloride, a hydrobromide, and a hydriodide which can be isolated.

Furthermore, sugars show their basic properties² in forming complex salts, as Rosenheim³ has pointed out. We are, therefore, justified in concluding that sugars do form a very small amount of salt in acid solutions. Of course the cane-sugar is such a weak base that these salts would be nearly completely hydrolyzed.

The relation between the concentrations of the sugar, acid and salt formed are expressed as follows:



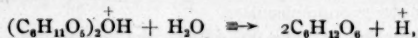
or

$$(\text{C}_b - x) \times C_H = K_{hyd} C_s = \frac{K_w}{K_b} C_s$$

$$\text{and} \quad (\text{C}_b - x) \times C_H \times C_{Cl} = \frac{K_{affn} K_w}{K_b} C_m, \quad (2)$$

in which C_b represents the initial concentration of the sugar, C_s the concentration of the complex sugar cation at the moment considered, and C_m that of the undissociated complex sugar salt. The amount of sugar changed into salt is so small that $(\text{C}_b - x)$, C_H and C_{Cl} have practically the value which they would have if no salt were formed.

If, now, the complex sugar cation is hydrolyzed by the water according to the following equation, in which C_s and $(\text{C}_{H_2\text{O}} - x)$ represent



or

¹ Bouchardat: Compt. rend., **74**, 866. Ann. Chim. Phys. [4], **27**, 145.

² Peligot: Compt. rend., **7**, 106. Ann. Chim. Phys. [2], **67**, 113; Violette: Compt. rend., **76**, 485. Maumené: Bull. Soc. Chim. [2], **19**, 289.

³ Ber. d. chem. Ges., **34**, 3377; **35**, 1115; **36**, 1833; **37**, 3662; **38**, 2777.

$$\frac{-dC_s}{dt} = \frac{dx}{dt} = K_{trans}C_s \times (C_{H_2O} - x), \quad (3)$$

the concentration of the cation and the water at any given moment, it follows from (2) that we can substitute for C_s the value

$$\frac{K_b}{K_w} (C_b - x) \times C_H$$

and we then get

$$\frac{dx}{dt} = K_{trans} \frac{K_b}{K_w} (C_b - x) \times C_H \times (C_{H_2O} - x), \quad (4)$$

which is actually what is found experimentally.

But if the undissociated salt were the substance undergoing hydrolysis,



or

$$\frac{-dC_m}{dt} = \frac{dx}{dt} = K_{trans}C_m \times (C_{H_2O} - x), \quad (5)$$

it follows from (2) that we can substitute for C_m the value

$$\frac{K_b}{K_w K_{affn}} (C_b - x) \times C_H \times C_{Cl},$$

and we then get

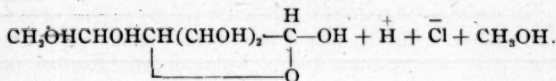
$$\frac{dx}{dt} = \frac{K_{trans} K_b}{K_w K_{affn}} (C_b - x) \times C_H \times C_{Cl} \times (C_{H_2O} - x), \quad (6)$$

in which $(C_b - x)$ is the concentration of the sugar at any moment and $(C_{H_2O} - x)$ is that of the water. In dilute solutions, $(C_{H_2O} - x)$ hardly changes in value, and the reaction appears to be monomolecular.

But equation (6) does not express the quantitative relations actually found to hold experimentally. It, therefore, follows that the undissociated salt, C_m , cannot be the substance which is chiefly undergoing hydrolysis, although it may do so to a small extent.

38
07
$$\text{CH}_2\text{OHCHOHCH}(\text{OC}_2\text{H}_5)_n$$
$$\text{CH}_2\text{OHCHONCH}(\text{CHOH})_2\text{COCH}_3,$$
$$\begin{array}{c} \text{CH}_2\text{OHCHONHCH(CHON)}_n\text{COCH}_3 + \overset{\text{H}}{\underset{|}{\text{O}}} + \bar{\text{Cl}} + \text{H}_2\text{O} \rightleftharpoons \\ | \quad \quad \quad | \\ \text{CH}_2\text{OHCHONHCH(CHON)}_n\text{C}^+\text{(OH)CH}_3 + \bar{\text{Cl}} + \text{H}_2\text{O} \end{array}$$

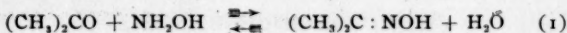
² Fischer: *Ibid.*, 26, 2400; 27, 2478.



ON THE REACTIONS OF CARBONYL COMPOUNDS WITH HYDROXYLAMINE AND WITH HYDROXYLAMINE HYDROCHLORIDE.

Theoretical.

Ketones and aldehydes react with hydroxylamine and form oximes. Nothing has been known up to this time of the rapidity or order of the reaction of various carbonyl compounds with the hydroxylamine. In Victor Meyer's¹ directions for making acetoxime from acetone and hydroxylamine, the mixture stood over night. We have found, however, that the reaction is practically finished in a few minutes at 100° and in 2 hours at 65°. The reaction is approximately one of the second order. Although the reaction certainly goes nearly to completion, it seems to be reversible.

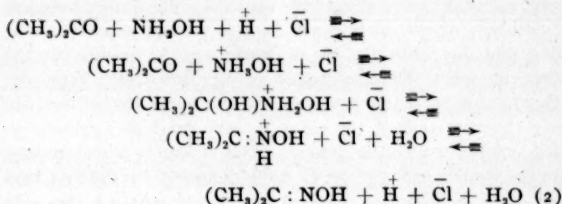


Since diethyl ketone reacts more slowly, and acetaldehyde more rapidly, with hydroxylamine than does acetone, it is probable that the so-called space interference influences these reactions. The velocity constant for the reaction between acetaldehyde and hydroxylamine in 0.1 N solutions at 10°.5 is 0.035. The constant for 0.1 N acetone and 0.1 N hydroxylamine at 1° is 0.0040, while at 65° it is 0.060. The constant for 0.1 N diethylketone and 0.1 N hydroxylamine at 35° is 0.005, while at 65° it is 0.010. These constants are calculated on the assumption that the reaction goes to completion. This is probably not true, as the reaction seems to be reversible; but the reaction goes so nearly to completion that only a small error is involved in the assumption made above.

When hydrochloric or hydrobromic acid is added to a mixture of acetone and hydroxylamine, the reaction progresses far more rapidly, just as is the case in ester catalysis, cane-sugar,

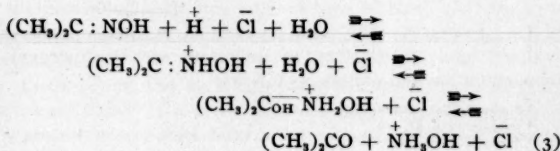
¹ Ber. d. chem. Ges., 18, 1324.

inversion, etc. This at once makes us suspect that the hydrochloric acid acts as a catalytic agent because it acts upon the base hydroxylamine and produces a greater concentration of the hydroxylammonium ions, which then react more rapidly with the acetone.



Strangely enough, however, when hydrochloric acid is added to accelerate the reaction the process does not go to completion as it practically does when no acid is present. The reason for this is now clear. In the presence of hydrochloric acid acetoxime is partly hydrolyzed into acetone and hydroxylamine hydrochloride. Janny's¹ statement that acetoxime is completely hydrolyzed by hydrochloric acid, and similar statements in text-books, are erroneous. We have found that a large excess of acid is not sufficient to hydrolyze the acetoxime completely. In fact there is always an equilibrium established and the equilibrium point is the same whether acetoxime is treated with a given amount of hydrochloric acid at a given temperature, or the equivalent quantities of acetone, hydroxylamine and hydrochloric acid are brought together under the same conditions.

Especially important, however, is the fact that a change in the amount of hydrochloric acid effects a change in the equilibrium in the system expressed in the following equation:



¹ Ber. d. chem. Ges., 16, 170.

The water is probably added to the double bond in all such reactions before the products of hydrolysis are formed. It has been found that an increase in the amount of hydrochloric acid causes a very decided increase in the amount of hydroxylamine hydrochloride, although the addition of several molecules of hydrochloric acid does not cause complete hydrolysis of the acetoxime. This is a very important case and probably, with the one of Bauer and Voermann,¹ is the confirmation of the ideas advanced by Acree and Johnson,² that in some reversible reactions it will be found that a change in the concentration of the catalyzer will produce a change in the equilibrium of the system. That there is a real change in the equilibrium was shown quite definitely by the fact that the same equilibrium point is established whether the acid be added to acetoxime in solution or to the equivalent concentrations of acetone and hydroxylamine. The cause of this change in equilibrium is probably the following. The acetoxime is a very weak base, as has been established by Walker.³ There is, however, an error in Walker's work, due to the fact that he did not take into consideration the hydrolysis of the acetoxime and the formation of hydroxylamine hydrochloride which is far less hydrolyzed than the acetoxime. The acetoxime is a very weak base and its hydrochloride is greatly hydrolyzed in water solution. We have been able to show this by the simple process of titrating 0.1243 gram acetoxime in 10 cc. water containing methyl orange with 0.1 N hydrochloric acid; it requires only 0.25 cc. of the total molecular quantity, 17.00 cc., to give the solution a pink color. In the solution of the acetoxime and hydrochloric acid there can be only a small amount of the acetoxime cation, which could be calculated if the affinity constant of the base were known. If the data in the experimental portion were a little more accurate they could be used to determine the affinity constant of the acetoxime. The small amount of acetoxime cation is almost surely the substance in equilibrium with the hydroxylammonium ion and acetone as follows:

¹ *Z. physik. Chem.*, **82**, 467.

² *THIS JOURNAL*, **27**, 410.

³ *Z. physik. Chem.*, **4**, 330.



But the hydroxylamine is such a strong base that its hydrochloride is practically not hydrolyzed at all and reacts only faintly acid to methyl orange. The addition of more hydrochloric acid then causes the formation of more acetoxime cation from the acetoxime then present, but does not change appreciably the concentration of the hydroxylammonium ions then present. Since this acetoxime cation formed must change to conform to the equilibrium expressed above, more acetone and more hydroxylammonium ions must be formed from the acetoxime cation and water to restore the equilibrium. Since the hydroxylammonium ion is not appreciably changed into hydrogen ions and hydroxylamine, the change in equilibrium is accompanied by disappearance of the hydrogen ions. Of course the real equilibrium between the acetoxime cation and the acetone and hydroxylammonium ion is not changed, but the apparent equilibrium between the acetone, total hydroxylamine, salt, and total acetoxime and salt is changed.

The fact that the equilibrium is changed in Tables XXIX. to XLII. by change in concentration of the acid is of very great importance in the theory of the catalytic influence of acids on reversible reactions. Practically the only well-known reversible reaction influenced catalytically by hydrogen ions is the reversible reaction between organic acids and alcohols on the one hand and esters and water on the other. In this reaction the equilibrium is not disturbed appreciably by change in the concentration of the hydrogen ions. The reason for this is that little of the hydrogen ions unites with either organic acid or ester, whereas in the work quoted above on the saponification of the oxime, nearly all of the hydroxylamine exists in the form of cations. This subject will be treated in detail in the section dealing with esterification and saponification.

Furthermore, the very interesting fact was established that the equilibrium in a given system changes with temperature. A rise in temperature from 10°.5 to 92° produces a gradual

increase in the amount of hydroxylamine hydrochloride and acetone necessary for equilibrium with the acetoxime hydrochloride, the equilibrium at the higher temperatures being established very quickly. A decrease in temperature brings about the reverse process, and the same equilibrium is found at a given temperature as was established when the temperature was rising. It is very probable that the decided apparent increase with rise in temperature in the affinity constant of acetoxime recorded by Walker is due to the above causes. With rise in temperature there is an increase in the amount of the hydroxylamine and its hydrochloride. Since hydroxylamine is a much stronger base than acetoxime, a greater percentage of the hydrogen ions disappear in the formation of hydroxylammonium ions at the higher temperature, and hence the acetoxime seemed to Walker to be a stronger base than it really is. The point is that at the higher temperature the hydrogen ions do not disappear in the formation of acetoxime cation, but in the formation of hydroxylammonium ions. The change in equilibrium with change in temperature may be the result of exothermic or endothermic reactions, or change in the affinity constant of the bases with change in temperature, or may come from other causes, which can only be determined by further work.

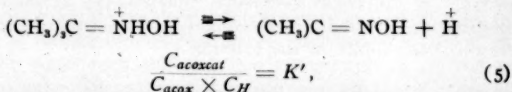
That there is really equilibrium between the acetone and hydroxylammonium ions on the one hand and the acetoxime cations on the other in a solution of these substances is shown further by the fact that the addition of acetone to the solution causes a decrease in the amount of hydroxylamine hydrochloride, whereas the addition of hydrochloric acid causes an increase in the concentration of the hydroxylamine hydrochloride and its ions. If equation (3) really represents the reaction we can express the equilibrium condition by equation (4),

$$\frac{C_{\text{acetone}} \times C_{\text{hydram}}}{C_{\text{acoxcat}}} = K, \quad (4)$$

in which C_{acetone} , C_{hydram} and C_{acoxcat} represent the concentrations of the acetone, hydroxylammonium ions and acetox-

ime cations, respectively. Now the concentrations of the acetone, hydroxylamine ions and total acetoxime and its salt can be determined analytically at any moment by the above method. But the value of $C_{acoxcat}$ can not be determined accurately by the analytical method employed in the present communication. A very close approximation can be made to it, however, when the concentrations of the acetone, hydroxylamine and hydrochloric acid have somewhere near the same values.

Since the acetoxime is a very weak base, the value of $C_{acoxcat}$ in the equilibrium equation,



is a very small part, probably only about 5 per cent of the value of C_{acox} , the concentration of the free base acetoxime. Instead of $C_{acoxcat}$ in equation (4) we can substitute

$$K' C_{acox} \times C_H,$$

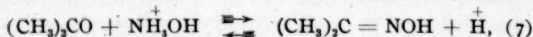
and we then get equation (6).

$$\frac{C_{acetone} \times C_{hydam}}{C_{acox} \times C_H} = KK' = K''. \quad (6)$$

That this equation holds very well experimentally is made evident by a glance at Tables XXV. to XLV. The value of K'' is about 1.25 when the concentrations of the substances do not vary widely. But when an excess of acid is added, the value of the constant decreases considerably as was predicted. The reason for this is that with the addition of the acid the percentage of increase in C_H is much greater than the percentage of decrease in C_{acox} , and consequent increase in $C_{acetone}$ and C_{hydam} , and hence the value of K'' decreases. But if we knew the value of $C_{acoxcat}$ and could substitute the data in equation (4) there is hardly any doubt that, with a good analytical method, good constants could be obtained. The fact that equation (6) gives a fair constant, which decreases

with large increase in C_H , shows that equation (2) represents the real equilibrium conditions.

That equation (2) represents the real equilibrium condition which may be written simply in the following equation,



because the concentration of the water hardly undergoes change, is further shown by the data in Tables XI. to XVI. inclusive.

When acetone and hydroxylamine hydrochloride are brought together in equivalent quantities, equation (7) should represent the reaction, and the following differential equation should represent the course of the reaction.

$$\frac{dx}{dt} = K(A-x)^2 - K_1X_2. \quad (8)$$

A is the original concentration of the acetone and hydroxylamine in gram molecules per liter, x is the change in concentration of each in the time t , K is the velocity constant for the reaction on the left in equation (7) and K_1 the velocity constant for the reaction on the right. When acetoxime and acids are brought together and react according to equation (7) the same differential equation (8) can be used. Equation (8) can be written in the form:

$$\frac{dx}{dt} = K_1 \left\{ \frac{K}{K_1} (A-x)^2 - x^2 \right\} = K_1 \left\{ \frac{KA^2}{K_1} - \frac{2KAX}{K_1} + \left(\frac{K}{K_1} - 1 \right) x^2 \right\}$$

or

$$K_1 = \frac{2A}{t} \sqrt{\frac{K}{K_1}} \log n$$

$$\frac{\left\{ 2x \left(\frac{K}{K_1} - 1 \right) - \frac{2KA}{K_1} - 2A \sqrt{\frac{K}{K_1}} \right\} \left\{ -\frac{2KA}{K_1} + 2A \sqrt{\frac{K}{K_1}} \right\}}{\left\{ 2x \left(\frac{K}{K_1} - 1 \right) - \frac{2KA}{K_1} + 2A \sqrt{\frac{K}{K_1}} \right\} \left\{ -\frac{2KA}{K_1} - 2A \sqrt{\frac{K}{K_1}} \right\}}$$

Reference to Tables XI. to XVI. shows that equation (9) gives as nearly a constant value for K_1 as the errors of the method will permit. A further discussion of this reaction will be given in a subsequent paper.

The action of carbonyl compounds on the free bases and salts of oximes, hydrazines, semicarbazides and amines is being continued in this laboratory.

EXPERIMENTAL.

Preparation of Acetoxime.

Twenty-five grams of hydroxylamine hydrochloride were dissolved in 30 cc. water at 5° and added to a solution of 15 grams of sodium hydroxide in 20 cc. water at 5°; 25 grams of acetone were then added. The temperature immediately rose to 45°. The mixture was then warmed for 30 minutes at 60°, and then cooled in ice. When the precipitate of acetoxime was filtered off and dried, it weighed 22 grams. When it was recrystallized twice from water it melted at 60° to 62°. 0.1243 gram in 10 cc. water required 0.25 cc. 0.1 N hydrochloric acid to give a pink color with méthyl orange.

Analytical Method.

In the two following tables there is given a general resumé of the experiments instituted to learn the best analytical method for the following reactions. It was apparent from the work of Adams¹ and Haga,² that the iodometric method is far better than the one involving the use of Fehling's solution. Since the work of Adams leaves no doubt that the use of sodium phosphate in the iodometric method is better than the use of sodium bicarbonate we carried out a number of experiments to ascertain the best concentrations of sodium phosphate, iodine, etc., for our purpose. The tables show how the amount of iodine required varies with the other conditions when the iodine is added to the hydroxylamine solution. Since the hydroxylamine reacts nearly quantitatively with the iodine according to the equation

¹ THIS JOURNAL, 28, 200.

² J. Chem. Soc., 51, 794.



one-half the molecular weight of hydroxylamine hydrochloride is the number of grams used in a liter to make the normal solutions.

The method finally adopted was the addition of about 10 cc. of the hydroxylamine solution to an excess of iodine in 10 cc. of 10 per cent sodium phosphate solution, and titration of the excess of iodine with 0.1 N sodium thiosulphate solution. The results are given in Table III. All the necessary check experiments were made to show that small quantities of sodium phosphate, sodium dihydrogen phosphate, acetoxime and acetone were without much influence on the titrations. The method is poor but is sufficiently accurate to make the preliminary study of the problem.

Table I.

Cc. 0.0851 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution.	Cc. 0.0858 N iodine required. Na_2HPO_4 .		
	0.3 gram.	0.5 gram.	Excess.
10	8.69	10.54	10.12
10	8.72		11.07
10	9.60		10.94
7		7.75	

Calculated 10 cc. = 9.96 cc. iodine.

Table II.

Cc. 0.1068 N $\text{NH}_2\text{OH} \cdot \text{HCl}$.	Cc. 0.0853 N iodine required. Na_2HPO_4 .					
	0.5 gram.	0.7 gram.	1 gram.	2 grams.	1 gram + 8 cc. 0.1 N KOH.	10 cc. 10 per cent solution.
10	12.65	12.65	13.41	13.66	13.00	12.87
10	12.02	12.67	13.39	13.83	12.96	13.13
10	12.19	12.65	13.15	13.82	12.95	13.10
10	12.21	12.74	13.20			13.06
10		12.85	13.20			13.07
10		13.15	13.28			12.97
10		12.96	13.20			
			12.82			
			12.85			

Calculated 10 cc. = 11.79 cc. iodine.

Table III.

Cc. 0.1008 N $\text{NH}_2\text{OH} \cdot \text{HCl}$.	Cc. 0.0853 N iodine required.
10	13.38
10	13.19
10	13.31
10	13.19

Calculated 10 cc. = 11.79 cc. iodine.

In all of the following work on the reactions between carbonyl compounds and hydroxylamine, the amount of hydroxylamine, or its hydrochloride, left unchanged in 10 cc. of the solution, corresponds to the number of cc. iodine required. Since the tables give also the amount of iodine required for the total hydroxylamine added, or for that formed by the complete hydrolysis of the acetoxime added, it is evident that these data enable us to calculate the concentrations of the acetone, hydroxylamine and acetoxime. In practically all cases the concentrations used are such that about 12.50 cc. 0.1 N iodine would be required to react with the total amount of hydroxylamine, free and combined. In order to save space, therefore, we have desisted from giving this enormous amount of data in the tables, and have furnished only the figures necessary to calculate the results.

Velocities of the Reactions between Hydroxylamine and Carbonyl Compounds.

The solution of hydroxylamine used in the following tables was made by treating 3.4725 grams $\text{NH}_2\text{OH} \cdot \text{HCl}$ with 50 cc. N NaOH and diluting to 500 cc. The acetone solution was made by diluting 1.466 grams acetone to 250 cc. with water. A is the number of cc. iodine solution used up by 10 cc. of the reaction mixture. Five cc. hydroxylamine solution used up 12.76 cc. iodine (A).

Table IV.

49.4 cc. 0.101 acetone solution and 50 cc. 0.1 N NH_4OH solution at 1° . $A = 12.67$ cc.

t .	0.0853 N iodine.	AK.
0.5	12.67	
2.1	12.67	
4.5	12.67	
118.0	10.05	0.0022
227.7	6.71	0.0039
304.5	5.50	0.0043

Table V.

49.4 cc. 0.101 N acetone solution and 50 cc. NH_4OH solution at 65° . $A = 12.76$.

t .	0.0853 N iodine.	AK.
1.0	12.60	(0.0127)
4.1	10.26	0.0585
8.0	8.42	0.0644
13.1	8.70	0.0354
30.1	6.14	0.035
65.0	2.87	0.053
105.5	1.72	0.060
148.2	1.15	0.068

Table VI.

50.3 cc. 0.0994 N $(\text{C}_2\text{H}_5)_2\text{CO}$ solution and 50 cc. 0.1 N NH_4OH solution at 35° . $A = 11.80$ cc.

t .	0.0882 N iodine.	AK.
5	11.49	0.0054
20	11.07	0.0033
41	9.71	0.0052
66	8.92	0.0049
86	8.24	0.0050
122	7.10	0.0054
173	6.23	0.0057

Table VII.

50.3 cc. 0.0994 N $(C_2H_5)_2CO$ solution and 50 cc. 0.1 N NH_2OH solution at 65° . $A = 12.45$ cc. Correction: 5 cc. $(C_2H_5)_2CO$ solution used 0.56 cc. 0.0882 N iodine solution.

<i>t.</i>	0.0882 N iodine.	AK.
1	12.31	0.011
5.5	11.72	0.011
20.1	10.10	0.011
39.1	8.38	0.012
63.1	8.24	0.008
91.9	7.88	0.010
142.5	4.77	0.011
221.0	3.73	0.0105
2880.0	1.37	

Table VIII.

1.142 grams CH_3COH diluted to 250 cc. Of this solution 48.15 cc. is equivalent to 50 cc. NH_2OH solution. 5 cc. CH_3COH solution used up 0.50 cc. iodine at 35° .

48.15 cc. 0.104 N CH_3COH solution and 50 cc. 0.1 N NH_2OH at 10.5° . $A = 12.06$ cc.

<i>t.</i>	0.0882 N iodine.	AK.
5.9	10.72	0.029
15.7	8.01	0.036
34.5	5.67	0.035
55.2	4.19	0.036
81.3	2.34	0.053

Table IX.

48.15¹ cc. 0.104 N CH_3COH solution and 50 cc. 0.1 N NH_2OH solution at 35° . $A = 11.90$ cc.

<i>t.</i>	0.0882 N iodine.
1	9.58
3.66	4.46
6.3	1.27
11.5	1.87
35.8	1.30

On the Hydrolysis of Acetoxime by Water and Acids, and the Equilibrium between Acetoxime Hydrochloride and Acetone and Hydroxylamine Hydrochloride.

In order to learn the rapidity of hydrolysis of acetoxime by water and acids and the equilibrium point between the acetoxime or its hydrochloride, and the acetone and hydroxylamine or its hydrochloride the following experiments were instituted. The results show that the equilibrium point changes with temperature. The bearing of this has been discussed in the theoretical portion.

In making the solutions 3.6789 grams of acetoxime were diluted to 500 cc. with water; 50 cc. of this solution were mixed with 50.38 cc. 0.1 N hydrochloric acid solution for hydrolysis. Ten cc. of the mixture were withdrawn at each time period and run into an excess of 0.0853 N iodine and 10 cc. of 10 per cent disodium hydrogen phosphate solution kept at 0°. The excess of iodine was titrated with sodium thiosulphate solution. Column II. gives the amount of iodine used up by the hydroxylamine, or its hydrochloride, formed.

Table X.

Hydrolysis of acetoxime with water alone. 0.3659 gram acetoxime was diluted to 100 cc. with water and the temperature kept at 65°.

<i>t.</i>	Cc. iodine 0.0882 N.
0	1.18
126	0.73
1 day	0.91
4 days	0.71

To 10 cc. was added 1 cc. 0.1 N hydrochloric acid solution, and the mixture was heated 30 minutes at 65°. The solution then required 3.44 cc. of iodine solution.

Table XI.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HBr at 2°.

t.	0.0853 N iodine.
1	0.41
2	0.66
3	0.76
5	0.90
9	1.20
12	1.20
18	1.41
22	1.59
35	2.08

Table XII.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HBr at 3°.

 $\frac{K}{K_1} = 0.197$. A = 13 cc. 0.0853 N iodine solution.

t.	0.0853 N iodine.	K_1 .
5	0.88	0.0029
15	1.76	0.0018
34	2.23	0.0011
48	2.51	0.00096
61	2.88	0.00095
93	3.67	0.0011
120	3.66	
338	4.00	
426	3.81	

Table XIII.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HBr at 11°.

 $\frac{K}{K_1} = 0.269$. A = 13 cc. 0.0853 N iodine solution.

t.	0.0853 N iodine.	K_1 .
2	0.96	0.0050
4	1.22	0.0032
7.1	1.55	0.0024
10	2.70	0.0035
15	2.76	0.0025
21	3.94	0.0036
25.5	4.30	0.0046
38	4.16	0.0024
60	4.44	

Table XIV.

55.5 cc. acetone (1.466 gram to 250 cc.) and 50 cc. $\text{NH}_2\text{OH} \cdot \text{HCl}$
(3.4725 gram to 500 cc.) at 13.5° . $A = 12.75$ cc.

<i>t</i> .	0.0853 N iodine.
0.88	9.27
1.67	8.20
5.5	7.04
9.0	5.54
15.33	4.71
20.5	4.83
24.67	4.13
48.12	5.01
148.5	5.01

Table XV.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HBr at 27° .

<i>t</i> .	0.0853 N iodine.
1.16	1.45
2.0	2.15
2.5	2.48
6.0	4.19
9.5	4.86
14.0	5.06
17.5	5.13
21.5	5.12
29.5	5.05

Table XVI.

Suppression by KBr. 50 cc. acetoxime solution, 50.38 cc.
0.1 N HBr, and 5.9555 grams KBr (10 mols.) at 27° .

<i>t</i> .	0.0853 N iodine.
1	1.47
2	2.24
4	3.45
6	4.23
7	4.44
8.08	5.08
10	5.27
15	5.68
31	5.09

Table XVII.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HBr at 50°.

<i>t.</i>	0.0853 N iodine.
1	4.44
2	5.69
10	5.97
20	5.97
45	5.95

Table XVIII.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HCl at 27°.

<i>t.</i>	0.0853 N iodine.
1.0	1.87
1.5	2.10
2.5	3.05
4.0	3.65
5.25	4.04
7.16	4.79
10.16	5.39
15.0	5.26
31.0	5.87

When 10 cc. were withdrawn and treated to boiling for a short time 8.72 cc. of iodine solution were required. The remainder of the above mixture was heated to 90°. *t* = time after reaching 90°.

<i>t.</i>	0.0853 N iodine.
5	7.15
20	7.08

This last table shows the change of equilibrium with change in temperature.

Table XIX.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HCl at 50°.

<i>t.</i>	0.0853 N iodine.
5	5.60
10	6.08
15	6.13
20	6.01
30	6.01
45	6.15
80	6.25

Table XX.

Suppression by KCl, 50 cc. acetoxime solution, 50.38 cc. 0.1 N HCl, and 3.73 grams KCl (10 mols.), at 27°.

<i>t.</i>	0.0853 N iodine.
1.16	1.80
2.42	2.79
4.06	4.02
5.67	4.15
7.5	4.58
9.06	5.29
14.25	5.31
23.8	5.20
38.75	5.55

Table XXI.

To 47.8 cc. acetone solution (1.5166 grams in 250 cc.) was added 50 cc. $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution (3.4725 grams in 500 cc.) at 65°. A = 12.50 cc. 0.0882 N iodine.

<i>t.</i>	0.0882 N iodine.
5.33	6.76
7.1	6.80
37.33	6.56
102.0	6.84

Table XXII.

To the 55.8 cc. left of the above mixture 4.2 cc. 1.05 N HBr at 65°.

<i>t.</i>	0.0882 N iodine.
1.0	7.76
4.1	8.06
7.8	8.51
43.6	8.15

Equilibrium was thus changed by a change in concentration of the acid present.

In the 3 following tables the concentrations are: 1.5166 grams of acetone diluted to 250 cc.; 3.4725 grams hydroxylamine hydrochloride to 500 cc.

Table XXIII.

47.8 cc. acetone solution and 50 cc. $\text{NH}_4\text{OH} \cdot \text{HCl}$ solution at 65° . $A = 12.59$ cc. 0.0882 N iodine solution.

t	0.0882 N iodine.
0.8	6.69
1.5	6.76
2.5	6.81
6.0	6.83
1440.0	6.94

Table XXIV.

47.8 cc. acetone solution and 50 cc. $\text{NH}_4\text{OH} \cdot \text{HCl}$ solution at varying temperatures. At 65° . $A = 12.59$ cc.

Temp.	Time.	0.0882 N iodine.
65°	2.8	6.50
80°	20	7.50
92°	46	7.81
80°	80	7.59
65°	102	6.63
35°	285	5.80
10.5°	181	4.81

Change in Equilibrium with the Change in Concentration of the Acetone.

The following experiments were tried in order to study the change in equilibrium produced by change in the concentration of the acetone. The amount of hydroxylamine hydrochloride was constant. The value of K gives the approximate constant obtained by substituting the proper data in the formula

$$\frac{(\text{CH}_3)_2\text{CO} \times \overset{+}{\text{NH}_4\text{OH}}}{(\text{CH}_3)_2\text{C}=\text{NOH} \times \overset{+}{\text{H}}} = K,$$

as was discussed in the theoretical portion. In the small parentheses in the headings above the tables the *molecular*

quantities of acetone are placed under the term 0.5 amount, etc.; the amount of hydroxylamine hydrochloride used is the unit of comparison.

Table XXV.

24 cc. 0.101 N acetone solution (0.5 amount acetone), 26 cc. water, and 50 cc. $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution (3.4725 grams to 500 cc.) at 65° . $A = 12.50$ cc. 0.0882 N iodine.

<i>t.</i>	0.0882 N iodine.
3	8.80
12.2	8.75
21.75	8.80
28	8.76
Mean,	8.75
	$K = 1.5$

Table XXVI.

25 cc. 0.1 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ and 25 cc. 0.1 N acetone (1 amount acetone) at 65° .

<i>t.</i>	0.0882 N iodine.
5	6.76
7	6.80
102	6.84
Mean,	6.80
	$K = 1.4$

Table XXVII.

15 cc. 0.5 N acetone (3 amounts acetone), 10 cc. water, and 25 cc. 0.1 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ at 65° . $A = 12.50$ cc.

<i>t.</i>	0.0882 N iodine.
6.1	(3.15)
13	3.57
19.7	3.43
45.8	3.48
Mean,	3.50
	$K = 1.2$

Table XXVIII.

25 cc. 0.5 N acetone, (5 amounts acetone), 25 cc. 0.1 N $\text{NH}_2\text{OH}.\text{HCl}$ at 65° . A = 12.50 cc.

t.	0.0882 N iodine.
5.2	2.26
24.3	2.26
84.1	2.21
	Mean, 2.24
	K = 1.1

Change in Equilibrium with Change in the Concentration of the Hydrochloric Acid.

As was discussed in the theoretical portion, if there is real equilibrium between the acetoxime hydrochloride, and the acetone and hydroxylamine hydrochloride, this same equilibrium point should be attained whether acetoxime be treated with hydrochloric acid or acetone be heated with hydroxylamine hydrochloride. The equilibrium should, furthermore, be changed by a change in the concentration of the hydrochloric acid. In general, this idea is perfectly well established by the following experimental data. The formula

$$\frac{(\text{CH}_3)_2\text{CO} \times \text{NH}_2\text{OH}^+}{(\text{CH}_3)_2\text{C}=\text{NOH}^+ \times \text{H}} = K$$

seems to hold very well for those solutions containing amounts of acetone, hydroxylamine, hydrochloric acid and acetoxime having similar concentrations.

Acetone + $\text{NH}_2\text{OH}.\text{HCl}$
HCl varied.

Acetoxime + HCl
HCl varied.

Table XXIX.

(0.2 HCl)

20 cc. 0.1 N KOH, 5 cc. 0.5 N acetone, and 25 cc. 0.1 N $\text{NH}_4\text{OH.HCl}$ at 65° .

<i>t.</i>	0.0882 N iodine.
6	(2.80)
23	2.44
99	2.38
Mean,	2.41

Table XXX.

(0.2 HCl)

25 cc. 0.1 N acetoxime (0.73 gram to 100 cc.), 5 cc. 0.1 N HCl, and 20 cc. H_2O at 65° .

<i>t.</i>	0.0882 N iodine.
6.5	2.96
18.5	2.53
73.5	2.82
Mean,	2.89

Table XXXI.

(0.6 HCl)

5 cc. 0.5 N acetone, 10 cc. H_2O , 10 cc. 0.1 N KOH, and 25 cc. 0.1 N $\text{NH}_4\text{OH.HCl}$ at 65° .

<i>t.</i>	0.0882 N iodine.
7	4.97
17	5.02
40	5.05
Mean,	5.01
	$K = 1.35$

Table XXXII.

(0.6 HCl)

25 cc. 0.1 N acetoxime, 15 cc. 0.1 N HCl, and 10 cc. H₂O
at 65°.

<i>t.</i>	0.0882 N iodine.
10	5.07
33	4.85
145	5.00
Mean,	4.97

Table XXXIII.

(1 HCl)

25 cc. 0.1 N acetone and 25 cc. 0.1 N NH₂OH.HCl at 65°.

<i>t.</i>	0.0882 N iodine.
5	6.76
7	6.80
102	6.84
Mean,	6.80
K =	1.4

Table XXXIV.

(1 HCl)

25 cc. 0.1 N acetoxime and 25 cc. 0.1 N HCl at 50°.

<i>t.</i>	0.0882 N iodine.
15	6.13
45	6.15
80	6.25
Mean,	6.17

Table XXXV.

(1.4 HCl)

10 cc. H_2O , 5 cc. 0.5 N acetone, 10 cc. 0.1 N HCl, and 25 cc
0.1 N $NH_4OH.HCl$ at 65° .

<i>t.</i>	0.0882 N iodine.
8.5	7.29
21	7.30
66	7.37
109	7.43
	Mean, 7.35
	K = 1.06

Table XXXVI.

(0.8 HCl)

20 cc. 0.1 N HCl, 5 cc. H_2O , and 25 cc. 0.1 N acetoxime
at 65° .

<i>t.</i>	0.0882 N iodine.
6	5.63
27.33	5.74
49	5.67
	Mean, 5.68
	K = 1.1

Table XXXVII.

(1.8 HCl)

5 cc. 0.5 N acetone, 20 cc. 0.1 N HCl, and 25 cc. 0.1 N NH_4OH .
HCl at 65° .

<i>t.</i>	0.0882 N iodine.
7	8.00
27	7.96
54	7.94
	Mean, 7.96
	K = 0.94

Table XXXVIII.

(1.8 HCl)

4.5 cc. N HCl, 20.5 cc. H₂O, and 25 cc. 0.1 N acetoxime at 65°.

<i>t</i>	0.0882 N iodine.
7	7.64
23.5	7.76
141	7.80
Mean,	7.75

Table XXXIX.

(3 HCl)

5 cc. 0.5 N acetone, 5 cc. N HCl, 15 cc. H₂O, and 25 cc 0.1 N NH₄OH.HCl at 65°.

<i>t</i>	0.0882 N iodine.
11	8.30
29	8.35
41	8.44
142	8.37
Mean,	8.34
K =	0.58

Table XL.

(2.5 HCl)

6.25 cc. 1.0 N HCl, 18.75 cc. H₂O, and 25 cc. 0.1 N acetoxime at 65°.

<i>t</i>	0.0882 N iodine.
12	(8.02)
21	8.39
47	8.34
70	8.44
Mean,	8.39
K =	0.68

Table XLI.

(17 HCl)

5.21 cc. 7.68 N HCl, 5 cc. 0.5 N acetone, 14.79 cc. H₂O, and 25 cc. 0.1 N NH₂OH.HCl at 65°.

<i>t.</i>	0.0882 N iodine.
15	9.94
45	10.26
Mean,	10.10

Table XLII.

(5 HCl)

12.5 cc. N HCl, 12.5 cc. H₂O, and 25 cc. 0.1 N acetoxime at 65°.

<i>t.</i>	0.0882 N iodine.
5.33	8.54
20	8.52
54	8.44
Mean,	8.50

The three following tables give a resumé of the chief results obtained at 65°. In the first table the upper column gives the number of cc. used for the titration. The solution was 0.1 N with respect to the hydroxylamine hydrochloride, and the concentration of the acetone was 0.5, 1, 3 or 5 times 0.1 N, as indicated in the second column. The third column gives the number of cc. iodine required to oxidize the hydroxylamine, or its salt.

Table XLIII.

Cc. solution	10	10	10	10
Molecules acetone	0.5	1	3	5
Cc. iodine required	8.77	7.44	3.49	2.24

The second table shows the change in equilibrium with a change in concentration of the hydrochloric acid.

Table XLIV.

Cc. solution:

0.1 N $\text{NH}_2\text{OH} \cdot \text{HCl}$

+ 0.1 N acetone

Molecules HCl

Cc. iodine required

10	10	10	10	10	10	10
0.2	0.6	1.0	1.4	1.8	3	17
2.41	5.01	6.80	7.35	7.96	8.34	10.10

The third table gives the equilibrium attained when 0.1 N acetoxime is treated with varying amounts of hydrochloric acid. For a given amount of hydrochloric acid the equilibrium point is practically the same as it is in Table XLIV.

Table XLV.

Cc. solution:

0.1 N acetoxime

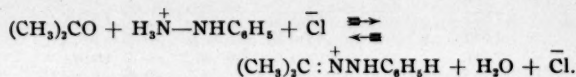
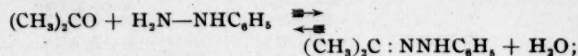
+ HCl Molecules HCl

Cc. iodine required

10	10	10	10	10	10	10
0.2	0.6	0.8	1.0	1.8	2.5	5
2.89	4.97	5.68	6.17	7.75	8.39	8.50

ON THE REACTION OF ACETONE WITH PHENYLHYDRAZINE AND
PHENYLHYDRAZINE HYDROCHLORIDE.

A preliminary announcement is made of the study of the action of acetone on phenylhydrazine, and on its hydrochloride. After the results of the action of acetone on hydroxylamine had been obtained it was seen that the reaction of carbonyl compounds with hydrazines, and with their salts, might be reversible. The idea seems to be confirmed by the experimental data.



The method of following the reaction was that of Meyer.¹ It does not seem to work well in the case under consideration, but further study may lead to improvement. The two following

¹ J. prakt. Chem. [2], 36, 115.

tables show that while the reaction between phenylhydrazine and acetone seems to go nearly to completion,¹ the phenylhydrazine hydrochloride reacts at most only very slowly with the acetone, and the reaction seems to be reversible. The changes are very slow in comparison with those between acetone and hydroxylamine or its hydrochloride. The work will be continued and the results reported must be considered only tentatively.

Table I.

50 cc. phenylhydrazine solution (2.7028 grams in 250.26 cc.), 40 cc. water, and 10 cc. 0.5 N acetone at 27°.

<i>t.</i>	Cc. iodine required for 10 cc. solution.	Cc. iodine solution required for 5 cc. phenylhydrazine solution at 22°.
0	17.88	17.88
5	13.62	...
24	11.82	...
40	10.30	...
184	9.46	...
1374	5.47	...
4252	2.72	...
5856	2.04	...
8907	1.62	15.09

Table II.

50 cc. phenylhydrazine hydrochloride solution (3.6113 grams in 250 cc), 40 cc. water, and 10 cc. 0.5 N acetone at 27°.

<i>t.</i>	Cc. iodine required for 10 cc. solution.	Cc. iodine solution required for 5 cc. phenylhydrazine hydrochloride solution at 22°.
0	17.23	17.23
2	17.23	...
2722	13.63	15.97
4309	13.13	...
7381	13.17	16.93

ON THE FORMATION AND SAPONIFICATION OF ESTERS AND THE THEORY OF REVERSIBLE CATALYTIC REACTIONS.

The theory of the reversible reaction between organic acids

¹ Strache: Monats. Chem., 12, 524.

and alcohols on the one hand and the esters and water on the other, has been discussed in some detail by Zengelis,¹ Euler,² Lapworth,³ Mellor,⁴ Kastle,⁵ Goldschmidt,⁶ Acree and Johnson,⁷ and especially by Stieglitz.⁸ While the theories held by individuals vary somewhat in detail they all have as a basis the general idea that intermediate products are directly concerned in the reactions. The writers wish to discuss the matter further in the light of some work done on the urazoles.

The experimental data of Berthelot and Gilles,⁹ Menschutkin,¹⁰ Goldschmidt, Ostwald,¹¹ Guldberg and Waage,¹² Wijs,¹³ Knoblauch¹⁴ and Kistiakovsky,¹⁵ amply prove that the saponification of esters in dilute water solution takes place according to the equation,

$$\frac{dx}{dt} = K_{\text{tran.}} \times C_{\text{ester}} \times C_{H_2O} \times C_H.$$

What is the mechanism of the reaction? It is well known that esters are weak bases and form salts with acids. Baeyer¹⁶ and Villiger isolated salts formed by the union of the esters of acetic, benzoic and oxalic acids with hydroferrocyanic acid and hydroferriocyanic acid. Rosenheim¹⁷ and his students proved that esters show their basic properties by forming double salts with antimony pentachloride and stannic chloride. Walker, Archibald, Steele and McIntosh¹⁸ showed that esters unite with liquid hydrochloric acid and form salts which are

¹ Ber. d. chem. Ges., **34**, 1901.

² Z. physik. Chem., **36**, 405, 663; **40**, 501; **47**, 356.

³ See Mellor's "Chemical Statics and Dynamics," 1904, p. 289.

⁴ *Ibid.*

⁵ THIS JOURNAL, **19**, 894. P. Am. Assoc. Adv. Sci., **47**, 238.

⁶ Ber. d. chem. Ges., **28**, 3218; **29**, 2208; **30**, 711.

⁷ THIS JOURNAL, **37**, 410.

⁸ Congress of Arts and Science, St. Louis, 1904, **4**, 276.

⁹ Ann. Chim. Phys. [3], **65**, 385; [3], **66**, 5; [3], **68**, 225; Compt. rend., **53**, 474, etc.

¹⁰ Ann. Chim. Phys. [5], **30**, 289; [5], **33**, 14; [5], **30**, 81, etc.

¹¹ J. prakt. Chem., [2], **28**, 449.

¹² *Ibid.* [2], **19**, 82.

¹³ Z. physik. Chem., **11**, 492; **12**, 514.

¹⁴ *Ibid.*, **22**, 268.

¹⁵ *Ibid.*, **27**, 250.

¹⁶ Ber. d. chem. Ges., **34**, 2692, 4189.

¹⁷ *Ibid.*, **34**, 3377; **35**, 1115; **36**, 1833; **37**, 3662; **38**, 2777.

¹⁸ Z. physik. Chem., **55**, 129. Phil. Trans., **205**, 99. J. Chem. Soc., **85**, 919, 1098; **87**, 784, 1013. Ber. d. chem. Ges., **34**, 4115. J. Am. Chem. Soc., **27**, 26; **28**, 588.

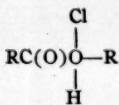
dissociated in the liquid hydrochloric acid. They expressed the opinion that the ester unites with a hydrogen ion and forms a complex cathion. A large amount of work on other carbonyl compounds, already referred to in this paper, leaves no doubt that esters form small quantities of salts in acid solutions, and the work of Coehn¹ on dimethylpyrone hydrochloride makes it probable that the ester forms part of the cathion. Finally, the writers have been able to show that the addition of small quantities of methyl acetate, ethyl acetate, methyl benzoate, 1-phenyl-3-ethoxyurazole, 1-phenyl-3,5-diethoxyurazole, or benzaldehyde to alcoholic or aqueous hydrochloric acid causes a lowering of the conductivity sufficient to indicate the formation of small amounts of ester salts in solution. The following table gives the data obtained:

Substance.	Amount of substance added to 25 cc. solution.	Solution used.	Decrease in conductivity. Per cent.
Ethyl acetate	0.1 cc.	0.1 N alcoholic hydrochloric acid	1.6
Methyl benzoate	0.1 cc.	0.1 N alcoholic hydrochloric acid	0.8
Benzaldehyde	0.1 cc.	0.1 N alcoholic hydrochloric acid	5.7
Benzaldehyde	0.2 cc.	0.1 N alcoholic hydrochloric acid	10.0
Phenyl-3-ethoxyurazole	0.05 gm.	0.1 N hydrobromic acid	1.1
Phenyl-3-ethoxyurazole	0.1 gm.	0.1 N alcoholic hydrochloric acid	2.7
Phenyl-3-ethoxyurazole	0.5 gm.	0.1 N alcoholic hydrochloric acid	10.6
Phenyl-3,5-diethoxyurazole	0.1 gm.	0.1 N alcoholic hydrochloric acid	3.3
Phenyl-3,5-diethoxyurazole	0.5 gm.	0.1 N alcoholic hydrochloric acid	7.9
Methyl acetate	0.1 cc.	0.1 N hydrobromic acid	1.0
Ethyl acetate	0.1 cc.	0.1 N hydrobromic acid	1.0

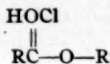
¹ Ber., d. chem. Ges., 35, 2673.

Furthermore, the decomposition of sulphonic esters¹ and urazole esters² by hydrochloric acid in which ethyl chloride is eliminated, indicates that the esters form hydrochlorides.

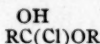
The constitution of these ester salts is a question of interest. Many of the workers in these fields are of the opinion that the salts are derivatives of tetravalent oxygen and have the formula I and II.



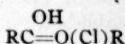
I.



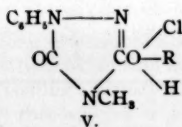
II.



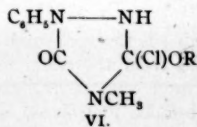
III.



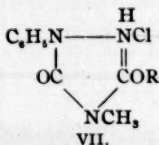
IV.



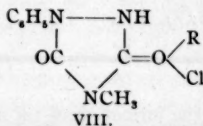
V.



VI.



VII.



VIII.

Since many esters and hydrochloric acid yield ethyl chloride formulas III. and IV. should also be considered and all four may be in tautomeric equilibrium. The urazole ester hydrochlorides may also exist in the form, V., VI., VII. and VIII. in equilibrium, with some one or two forms in preponderance.

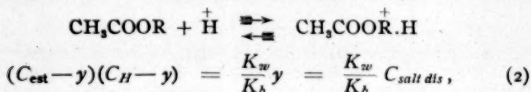
Since the esters then form salts it might be at once suspected that in the saponification of esters by water in the presence of acids the ester cation is saponified, just as the alkyl halides

¹ THIS JOURNAL, 19, 894.

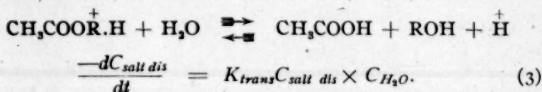
² Acree and collaborators: THIS JOURNAL, 27, 118; 31, 185; 32, 606; 37, 71, 361; 38, 1. Ber d. chem Ges., 35, 553; 36, 3139; 37, 184, 618.

react with anions, and acetamide cations and imido ester cations are hydrolyzed. Euler, Bredig,¹ Lapworth, Stieglitz, and Acree and Johnson have held that view, and many of the following equations have been developed by these writers, especially by Stieglitz. The equations are given here again, with others, to develop the entire subject.

If C_{est} gram molecules of ester and enough hydrochloric acid to give C_H gram ions of hydrogen ions are brought together in 1 liter of water we shall have the following reaction established very quickly, and get the equation



in which y is the very small amount of salt formed; the hydrogen ions from the water and small non-dissociated portions of the ester salt are disregarded. If now the ester cation is the substance hydrolyzed, we shall have, if we disregard the very small reverse reaction,



When the formation of the salt from the ester and hydrogen ions takes place very rapidly in comparison with the saponification of the ester cation, and the value of y is negligible in comparison with C_{est} and C_H we can substitute for $C_{salt\ dis}$

in equation (3) the value $\frac{K_b}{K_w} C_{est} \times C_H$ and we then get, as has been developed before in the other sections,

$$\frac{-dC_{salt\ dis}}{dt} = \frac{dx}{dt} = \frac{K_{trans} K_b}{K_w} (C_{est} - x) C_H \times (C_{H_2O} - x), \quad (4)$$

which is only another form of equation (1). This equation

¹ Z. Elek. Chem., 9, 118; 10, 586; 11, 528.

seems to hold whether the hydrogen ions come from water, weak acids or stronger acids. We have then harmony between the quantitative data and the idea that the ester cation *may* be the substance hydrolyzed. The ester exists in solution probably only as free base, cations and undissociated salt. The free base is hydrolyzed certainly only very slowly by the water as direct experiment shows. If the undissociated ester hydrochloride were the substance chiefly hydrolyzed we should have, as has been developed in the previous sections, the following equation expressing the reaction velocity:

$$\frac{dx}{dt} = \frac{K_{trans} K_b}{K_{affin} K_w} (C_{est} - x) \times (C_{H_2O} - x) \times C_H \quad (5)$$

Since the velocity of hydrolysis of esters is not proportional to the *square* of the concentration of the hydrogen ions, it is evident that the non-dissociated ester salt can not be greatly concerned in the saponification. Furthermore, since the free ester is not appreciably concerned in the reaction there is left only the ester cations, and this seems to be the substance which is really hydrolyzed. But the moment the hydrolysis of the ester begins the reverse reaction, the formation of the ester from the organic acid and the alcohol also begins.

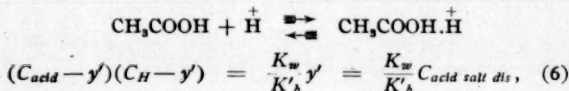
The reactions involved in formation of esters from organic acids and alcohols in the presence of hydrogen ions are probably exactly analogous to those involved in the saponification of the esters. Lapworth, Euler, Kastle, and Stieglitz have pointed out that the organic acids probably unite with the hydrogen ions to a small extent and that this complex organic acid cation reacts with the alcohol and forms the ester, water and hydrogen ions. There is no doubt that the organic acids do have weakly basic properties, just as many ureas, pyrimidines, urazoles and amides have both basic and acid properties. Rosenheim¹ found that organic acids behave like the esters, in their action on antimony pentachloride. Hell and Mühlhauser² found that acetic and other organic acids form unstable

¹ *Loc. cit.*

² *Ber. d. chem. Ges.*, **12**, 734.

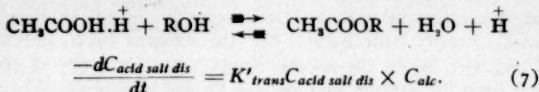
hydrobromides, such as $2\text{CH}_3\text{COOH.HBr}$. McIntosh¹ observed similar phenomena and Farmer² showed, too, that organic acids have basic properties.

If, then, the organic acid does actually unite with the hydrogen ions and form a cation, which reacts with the alcohol, we shall have the following equation holding under



exactly the same conditions which apply to the ester. K'_b is the affinity constant of the acetic acid as above, and y' is the small amount of cation formed, the molecular form of the salt being so small in amount as to be disregarded.

If the acid cation is the substance which reacts with the alcohol we shall have, if we again disregard the small amount of the reverse reaction,



But just as with the esters we can substitute for $C_{\text{acid salt dis}}$ in (7) the value $\frac{K'_b}{K_w} C_{\text{acid}} \times C_{\text{H}}$. We then get, as developed with the esters, equation (8) as representing

$$\frac{dx}{dt} = K'_{\text{trans}} \frac{K'_b}{K_w} (C_{\text{acid}} - x) \times (C_{\text{alc}} - x) \times C_{\text{H}}, \quad (8)$$

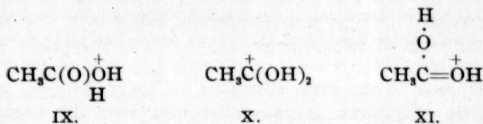
the reaction which should be found to hold experimentally if the organic acid first unites very rapidly with the hydrogen ions and forms a complex cation, $\text{CH}_3\text{COOH.H}^+$, which reacts slowly with the alcohol and forms ester, water and hydrogen ions. Equation (8) is actually found to represent the velocity

¹ J. Am. Chem. Soc., 28, 588.

² J. Chem. Soc., 83, 1440.

of formation of the esters. We are led, then, to the idea that the reversible reactions in the system, water, alcohol, ester, organic acid and hydrochloric acid are brought about by the formation and reactions of intermediate cathions produced by the union of hydrogen ions with the ester and organic acid.

Whether the acid cathion, $\text{CH}_3\text{COOH}^+\text{H}$, has the formula IX., X. or XI. need not be discussed.



When the system is in equilibrium just as much ester is formed as is saponified into organic acid. The two terms dx in equations (4) and (8) are, therefore, equal and we get, by substitution, equation (9) as representing the equilibrium conditions.

$$K_{trans} \frac{K_b}{K_w} C_{est} \times C_{H_2O} \times C_H = K'_{trans} \frac{K'_b}{K_w} C_{acid} \times C_{alc} \times C_H$$

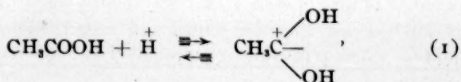
or

$$C_{est} \times KC_{H_2O} = K' C_{acid} \times C_{alc}. \quad (9)$$

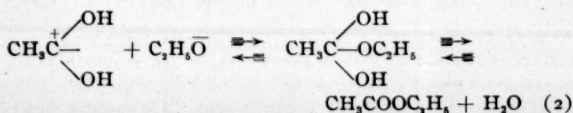
C_{est} , C_{H_2O} , C_{acid} and C_{alc} are the concentrations of these substances at the equilibrium point. C_H is the original concentration of the hydrogen ions less the very small amount united with the ester and organic acid. The equilibrium point is apparently independent of the concentration of the hydrogen ions.

To recapitulate then: The idea that the reversible reactions taking place in the system ester, water, acid, alcohol and hydrochloric acid are due to reactions of the complex cathions, formed by the union of a very small amount of the hydrogen ions with a small amount of the ester and organic acid, leads to equations which hold experimentally. The assumption explains, in equations (4) and (8), why the velocity of saponification and of esterification increases directly in proportion to the concentration of the hydrogen ions. It further makes clear, in

equation (9), the experimentally established fact that the equilibrium of the system is not appreciably changed by change in the concentration of the hydrogen ions. These ideas have already been developed by Euler, Lapworth, Kastle and especially by Stieglitz, and they have received very good experimental verification. Goldschmidt¹ has recently pointed out some discrepancies not entirely in harmony with the above equations and doubtless many others will be reported later. The assumption, however, gives a good working basis and may be used as a guide for the further work needed to clear up the whole matter. There is one very serious objection to an assumption common to the ideas advanced by Euler, Zengelis and Lapworth. Lapworth proposed the idea that the organic acid unites with the hydrogen ion,

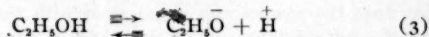


and that this product then reacts with the alcoholate ion as follows:

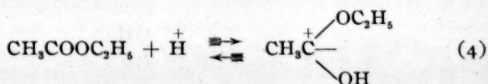


The objection is the following: The increase in the concentration of the hydrogen ions in the solution of the organic acid and alcohol to n times its former value would, it is true, cause the concentration of the organic acid cation in equation (1) to become approximately n times as great; if the concentration of the alcoholate ions in (2) were to remain the same then the reaction velocity would become n times its former value. But if the alcoholate ions come from the dissociation of the alcohol according to equation (3)

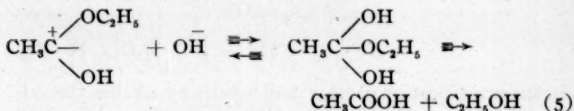
¹ Goldschmidt and Sunde: Ber. d. chem. Ges., **39**, 711.



the increase of the H^+ concentration to n times its former value would cause the concentration of the $\text{C}_2\text{H}_5\text{O}^-$ ions to become the n th part of its former value. The product of the alcoholate ions $\text{C}_2\text{H}_5\text{O}^-$, and the organic acid cations $\text{CH}_3\text{C}^+(\text{OH})_2$ in (2) would, therefore, not be changed at all and the reaction velocity, if Lapworth's explanation were correct, would remain unchanged with change in the concentration of the hydrogen ions. The same thing would hold true of the reverse reaction expressed as follows,

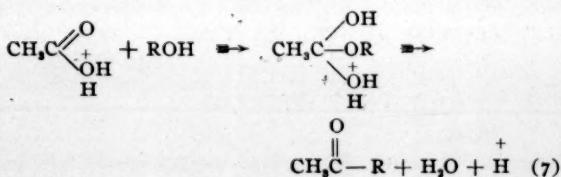
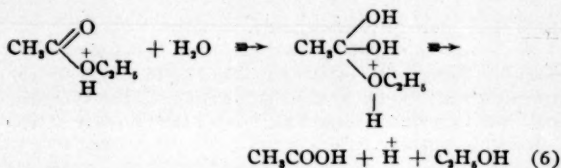


followed by the reactions in equation (5).

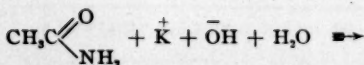
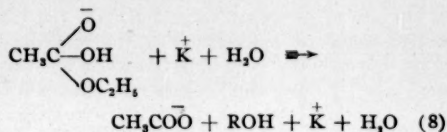
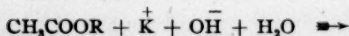


Although an increase in the concentration of the hydrogen ions to n times a former value would cause the concentration of the ester cation in (4) to become n times as great, yet this same increase in the concentration of the hydrogen ions would cause the concentration of the hydroxyl ions in (5) to become the n th part of its former value, and hence the velocity of the reaction would be independent of the concentration of the hydrogen ions. The same objection holds for certain assumptions made by Euler and Zengelis and these will be discussed later. Especially, however, must it be emphasized that the assumption of the ionization of acetic acid into acetyl and hydroxyl ions and CH_3CO^+ , OH^- , and of alcohol into ethyl and hydroxyl ions, C_2H_5^+ and OH^- , fails to meet the requirements of the mass law in the reactions under consideration. It is clear

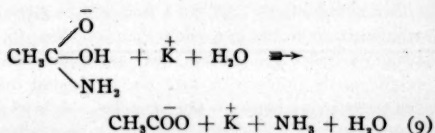
then that the alcohol and water react with the acid cation and the ester cation not as ions but as neutral molecules, just as the neutral ethyl iodide reacts with urazole ions, hydroxyl ions, etc. The water or alcohol is probably added to the carbonyl group in these reactions, but this is not certain.



In the saponification of esters and amides by alkalies the alkali probably attacks the carbonyl group. Euler¹ and others referred to above have shown that carbonyl compounds, such as aldehydes, have both basic and acid properties.

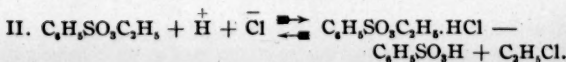
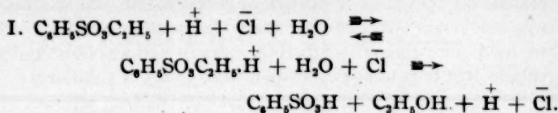


¹ Ber. d. chem. Ges., 38, 2551; 39, 344.



In the consideration of the hydrolysis and the formation of ordinary esters one phase of the work does not apply, but it must be developed for other esters.

Although the hydrochlorides of the ordinary esters do not decompose appreciably into the alkyl chlorides and the organic acids, some ester hydrochlorides do suffer this transformation along with the hydrolysis. A notable case is that of the sulphonic esters. When a sulphonic ester is treated with water and hydrochloric acid, two apparently independent side reactions take place. One is the hydrolysis of the ester into the sulphonic acid and the alcohol corresponding, and the other is the decomposition of the sulphonic ester hydrochloride into the alkyl chloride and the sulphonic acid.¹

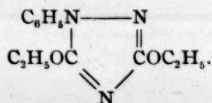


Evidently the amount of transformation through each of the reactions I. and II. depends upon the relative stability of the sulphonic ester cation towards water and the stability of the sulphonic ester hydrochloride. These 2 factors will doubtless vary with the ester, temperature and other conditions. Apparently, it should be possible to suppress the reaction I. and give reaction II. more opportunity to become the chief one by treating the sulphonic ester in alcoholic hydrochloric acid. This has been done with certain urazole derivatives.

¹ Kastle and Frazer: *THIS JOURNAL*, 19, 894.

We should then expect to find some esters, the cathions of which are so stable towards water that the esters would hardly undergo hydrolysis at all, but the hydrochlorides of which might easily decompose into the acids and an alkyl chloride. Such esters are those of the urazoles. A brief account of their properties will be given here, and a more detailed statement will be made later.

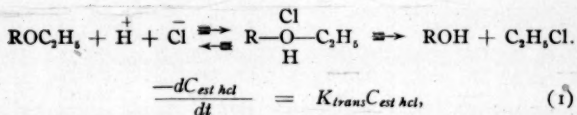
The 1-phenyl-3-ethoxyurazole is not saponified by aqueous hydrobromic acid, but is decomposed quantitatively by alcoholic hydrochloric acid into phenylurazole and ethyl chloride. Five cc. 0.0992 N hydrobromic acid and 0.1 gram phenyl-3-ethoxyurazole were heated 12 hours, at 100°. The solution then titrated against 5.00 cc. 0.0995 N potassium hydroxide in the presence of methyl orange and 10.00 cc. 0.0995 N potassium hydroxide in the presence of phenolphthalein. This shows that no hydrobromic acid was used in the formation of ethyl bromide and phenylurazole. The solution was acidified with sulphuric acid and extracted with chloroform. No phenylurazole was obtained, but when the chloroform filtrate was evaporated, 0.1 gram of 1-phenyl-3-ethoxyurazole, m. p. 148°, was recovered. In order to study the reaction quantitatively we used the 1-phenyl-3,5-diethoxyurazole and alcoholic hydrochloric acid in equimolecular quantities in 0.5 N solutions.



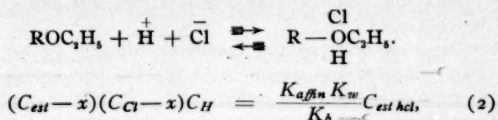
Since the 2,3-amide group is a much stronger acid than the 4,5-amide group it was predicted that the 5-ethoxy group would be a very much stronger base than the 3-ethoxy group and would unite with, and react with, the hydrochloric acid nearly to the exclusion of the 3-ethoxy group. This prediction was happily verified quantitatively by experiment. The reactions were carried out in small sealed tubes at 60°, and after the reaction was stopped the contents were poured into water in extraction funnels. The unchanged hydrochloric acid was titrated with standard alkali in the presence of methyl orange and the 1-

phenyl-3-ethoxyurazole formed was then titrated with standard alkali in the presence of phenolphthalein. The unchanged 1-phenyl-3,5-diethoxyurazole was extracted by means of chloroform and weighed.

If the urazole ester hydrochloride is decomposed directly we should have the reaction expressed by the following equations:



in which $C_{\text{est hcl}}$ is the concentration of the urazole ester hydrochloride at any moment. But the concentration of the ester hydrochloride can be expressed approximately, as has been developed several times above, in terms of the concentrations of the ester, hydrogen ions and chloride ions at any moment and can be represented by the equation



in which $(C_{\text{est}} - x)$, $(C_{\text{Cl}} - x)$ and C_{H} are the concentrations of the ester, chloride ions and hydrogen ions at any moment. We can, therefore, substitute for $C_{\text{est hcl}}$ in (1) its value in (2) and we then get equation (3)

$$\frac{-dC_{\text{est hcl}}}{dt} = \frac{dx}{dt} = \frac{K_{\text{trans}} K_b}{K_{\text{affin}} K_w} (C_{\text{est}} - x)(C_{\text{Cl}} - x)C_{\text{H}} = K(C_{\text{est}} - x)(C_{\text{Cl}} - x)C_{\text{H}}. \quad (3)$$

This equation will not hold exactly since the value of C_{H} does not remain constant as indicated in (3) but decreases to some extent because the urazole acid formed is weaker than hydro-

chloric acid. We should expect the value of K to decrease, and if the urazole acid formed were very weak, equation (3) would become practically trimolecular.

The following data, however, show, qualitatively, that the urazole ester actually does act upon the hydrochloric acid and form ethyl chloride. The experiments are given in a tabular form for convenience.

Time in minutes.	x .	$A - x$.	$AK = \frac{x}{t(A - x)}$.
15	0.528	0.472	0.075
32	0.706	0.294	0.075
60	0.741	0.259	0.048
180	0.913	0.087	0.058
Average,			0.064

As a consequence of this decomposition of the ester hydrochloride it has been impossible, as was predicted, to obtain the esters by heating the urazole acids with alcoholic hydrochloric acid.

This work on the urazole esters and sulphonic esters will be continued.

The discussion of the reversible reaction between esters, water, alcohol and organic acid has led to an understanding as to why the three so-called laws¹ of catalysis apply to this particular case. These laws may be expressed as follows:

(1) *When the catalyzer is not changed during the reaction it affects only the velocity of the reaction, but does not change the nature of the reaction or the apparent order of the reaction.*

(2) *The catalyzer affects the velocity constant directly in proportion to the concentration of the catalyzer.*

(3) *A change in the concentration of the catalyzer does not change the equilibrium point in reversible reactions.*

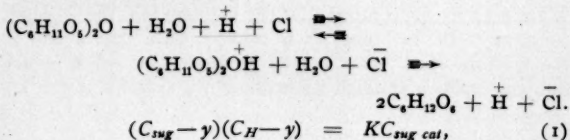
These three so-called laws have been found to hold so well for the esterification work that they have been assumed to hold for all catalytic reactions. The esterification work, the hydrolysis of amides, and the inversion of cane-sugar are prac-

¹ For an excellent discussion of catalysis see Herz "Die Lehre von der Reaktionsbeschleunigung durch Fremdstoffe," Ahren's Sammlung, Vol. XI, p. 103.

tically the only well-known cases in which a catalytic reaction has been well studied, and it is rather surprising that these three cases should be the basis of the above so-called laws. It will now be shown that these so-called laws are not laws at all, but apply only to certain special cases, and further that these so-called laws have no physical or chemical basis but are really only a brief statement of the results actually obtained experimentally. They cannot be used to make predictions concerning all catalytic reactions, but are only approximate expressions of special reactions.

There are two classes of reactions that must be considered in showing that these laws for catalysis by acids (or bases) do not hold: (1) (A) Simple reactions in which one reaction constituent is a strong base (or acid), and (B) reversible reactions in which a constituent of one reacting set of the substances is a much stronger base (or acid) than the corresponding base (or acid) in the opposing set of substances. (2) (A) Simple reactions in which the catalyzer affects the reaction velocity in proportion to the square, or other power of its concentration, and (B) reversible reactions in which the velocity of one reaction increases as the m power of the concentration of the catalyzer increases, while the velocity of the reverse reaction increases in proportion to the m power of the concentration of the catalyzer. These cases will be considered in the order given.

(1) If in a reaction one of the constituents is a comparatively strong base, such as ammonia, aniline, etc., and it enters into the reaction through the reaction of its cation with the other constituents, then the velocity of the total reaction cannot increase directly in proportion to the increase in the concentration of the hydrogen ions added. The consideration of the hydrolysis of cane-sugar will make this clear. In the hydrolysis of cane-sugar according to the following equation, the amount of hydrogen

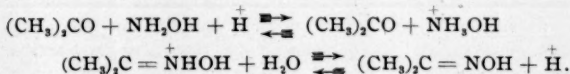


ions and of cane-sugar used to form the cane-sugar cation is so small that the concentrations of these two are hardly affected, and $(C_H - y)$ and C_H are practically equal. It follows, then, that if the concentration of the hydrogen ions added were made twice as great the $(2C_H - y')$ corresponding to the new conditions would be practically twice as great as before, and the new value of $C_{sug\ cat}$ would also be twice as great as before. The velocity of the reaction would then be twice as great, as we actually find by experience.

Suppose, however, that, even though the sugar did not react appreciably with water and form a cation of the corresponding base (ammonia and aniline are such cases), it could unite almost completely with a molecular quantity of hydrochloric acid, just as ammonia and aniline do. Then the addition of a quantity of hydrochloric acid equivalent to one-fourth of the cane-sugar would cause one-fourth of the cane-sugar to be changed into the corresponding cations and the reaction velocity would have a certain value. The addition of twice the amount of hydrochloric acid would cause nearly half of the cane-sugar to be changed into cation and the velocity constant would become nearly twice as great as before. The addition of one molecular quantity of hydrochloric acid would cause the concentration of the sugar cation and the velocity constant to become nearly four times the former value. Up to this point, then, the velocity constant would increase nearly directly in proportion to the increase in the amount of hydrochloric acid added. But the further addition of hydrochloric acid would not cause the corresponding increase in the velocity constant, because the cane-sugar would be already nearly completely converted into cations and the further addition of hydrochloric acid would cause only a slight increase in the concentration of the cations. In fact, the addition of much hydrochloric acid would cause a suppression of the ionization of the cane-sugar hydrochloride and hence a decrease in the concentration of the cations and the velocity constant of the reaction. It is evident, then, that if one of the reacting constituents is a fairly strong base which enters into the reaction through its cations the velocity of the re-

action cannot increase directly in proportion to the concentration of the acid added. Examples of this are the reactions between carbonyl compounds and hydroxylamine, the hydrolysis of amides by aqueous solutions of acids, and the hydrolysis of imido esters by acids. Under these conditions the second law of catalysis cannot hold. It can hold only in those cases in which the base is so weak that only a trace of the salt is formed; since these are the only cases studied up to this time it is not surprising that not much further thought was given to the matter.

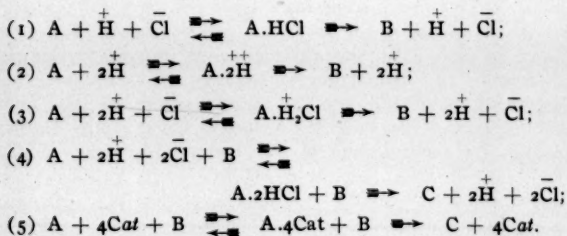
(2) The third law of catalysis cannot hold in those reversible reactions in which one constituent of one reaction is a strong base, while the corresponding constituent of the reverse reaction is a very weak base, provided the bases enter into the reactions through their cations or salts. This has already been discussed in the reversible reactions between carbonyl compounds and hydroxylamine and its hydrochloride. These reactions are accelerated by the addition of hydrochloric acid.



The acetoxime is a very weak base and hence unites with only a small part of the acid when one molecular quantity of hydrochloric acid is added. The addition of two molecular quantities of hydrochloric acid would cause the formation of nearly twice as much acetoxime cation and hence the velocity of the hydrolysis of the acetoxime cation should be nearly twice as great. But the addition of one molecular quantity of acid to the hydroxylamine changes the hydroxylamine practically completely into the hydroxylammonium ions, and the addition of two molecular quantities of acid would hardly change the concentration of the hydroxylammonium ions. It is evident, then, that the equilibrium in the system given above would be changed by the addition of more acid. Knowing that the acetoxime is the weak base, we could predict that the addition of more acid would cause the formation of more acetoxime cation from the acetoxime than in solution

but would cause no further appreciable formation of hydroxylammonium ions from the hydroxylamine then in solution. As a result, because of the equilibrium between the water and acetoxime cations on the one hand and the acetone and hydroxylammonium ions on the other the addition of more acid causes a change in the equilibrium of the system and results in the formation of more of the hydroxylammonium ions, or ions corresponding to the stronger base. We shall study this class of reactions in much more detail.

(3) The second law of catalysis cannot hold in those reactions in which changes are brought about by the union of very small amounts of two, three, or more ions, or molecules, of the catalyzing agent with a very small amount of some compound in the reaction system, which addition product then reacts with other constituents. This case has already been considered in the rearrangement of the acetylhalogenaminobenzene derivatives, into halogenacetanilide derivatives, where it was shown that the velocity of this catalyzed reaction increases as the *square* of the concentration of the hydrogen ions instead of as the first power demanded by the second law of catalysis. We can readily see that in some reactions involving some reaction similar to a hydrolysis we might have two, three or more ions, or molecules of the catalyzer uniting with some constituent and the further transformation of this addition product into other substances. The following equations will give some types of these reactions:

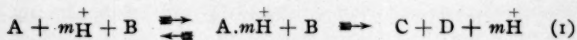


The first two reactions will increase in velocity directly in

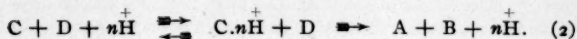
proportion to the *square* of the concentration of the hydrogen ions, the velocity of the third-reaction will increase in proportion to the third power of the concentration of the hydrogen ions and the velocity of the fourth and fifth reactions will increase in proportion to the fourth power of the concentration of the hydrogen ions or catalyzer.

(4) The third law of catalysis cannot hold in those reversible reactions in which the velocity of one reaction is accelerated in proportion to the m power of the concentration of the catalyzer while the velocity of the reverse reaction is accelerated in proportion to the n power of the concentration of the catalyzer. It is assumed, here, as in (3), that only very small amounts of the catalyzer unite with very small amounts of some other substance and that the addition product then undergoes further transformation.

As an illustration let us consider the following equations:



and



The velocity of the reaction can be represented by the equation (3)

$$\frac{dx}{dt} = K(C_A - x)(C_B - x)C_H^m - K'(C_C + x)(C_D + x)C_H^n. \quad (3)$$

When equilibrium is established we have

$$K(C_A - x)(C_B - x)C_H^m = K'(C_C + x)(C_D + x)C_H^n$$

or

$$\frac{K(C_A - x)(C_B - x)}{K'(C_C + x)(C_D + x)} = \frac{C_H^m}{C_H^n} = C_H^{n-m}. \quad (4)$$

There was a mistake on page 412 in the former article¹ by Acree and Johnson in that the term $(C_{cat})^{\frac{m}{n}}$ was by an over-

¹ THIS JOURNAL, 37, 410.

sight inserted instead of the expression C_{cat}^{m-n} . Since C_H^{n-m} in (4) varies with the change in the concentration of the hydrogen ions it is evident that the equilibrium between A, B, C and D must vary with the change in the concentration of the ions. In the work on esters $n-m$ becomes zero and C_H^{n-m} becomes unity, and the equilibrium is not appreciably changed by a change in the concentration of the catalyzer. It is evident that when n and m are equal, but not unity, the third law of catalysis holds, but the second does not.

The discussion in the preceding sections applies equally well to the reactions in which negative catalysis takes place. It is perfectly evident that the velocity of certain reactions, reversible or non-reversible, could be decreased because the catalyzer combines with some constituent of the reacting system and hence causes a decrease in the concentration of that constituent. The conditions for negative catalysis would be fulfilled if the addition product does not react directly with the other constituents, but is always in equilibrium with the catalyzer and the other component of the addition product, which component does react with the other constituents. The negative catalysis of the reaction between the phenylthiourazole anion and ethyl iodide by the hydrogen ions of hydrochloric acid is a very good example. The hydrogen ions unite with some of the phenylthiourazole anions, decrease the concentration of the phenylthiourazole anions and hence lower the velocity of the reaction. Since the phenylthiourazole formed, however, is always in equilibrium with the phenylthiourazole anions and the hydrogen ions, the reaction is not stopped short of completion at all, but only made slower. The general ideas discussed in the four preceding sections apply equally well to the formation of this non-reactive addition product, and hence to the negative catalysis by acids, bases and salts.

In the above discussion of catalysis no attention has been given to the consideration of the catalytic action of finely divided metals, or other substances, nor to the reactions brought about by enzymes. Both the metals¹ and enzymes probably

¹ Stock, Gomolka and Heynemann: Ber. d. chem. Ges., **40**, 532. Stock and Bodenstein: *Ibid.*, **40**, 570. Rowe: Z. physik. Chem., **89**, 41.

have the power of condensing the reaction substances on their surfaces and hence increasing the reaction velocity on account of this increase in concentration of the substances. Of course the enzymes and metals probably have also specific chemical¹ catalytic action. These cases in the study of catalysis will be reported on later, in more detail.

The ideas advanced concerning the catalysis by acids hold just as well for reactions influenced catalytically by bases and metallic alcoholates.

Conclusions.

1. Work on the reactions between urazoles and alkyl halides, on the rearrangement of acetylhalogenaminobenzene derivatives, on the reactions of carbonyl compounds with hydroxylamine and phenylhydrazine, on the inversion of cane-sugar, on the hydrolysis of amides, and on the formation and saponification of esters teaches us that acids, bases and salts may act as positive or negative catalyzers and cause a change (increase or decrease) in the velocity of a reaction because they bring about changes (increase or decrease) in the concentrations of the particular ions or molecules entering into the reaction.

2. The study of the rearrangement of acetylchloraminobenzene has shown that the second law of catalysis given above does not hold in all catalytic reactions.

3. The study of the reactions of carbonyl compounds with hydroxylamine has shown that the third law of catalysis given above does not hold in all catalytic reactions.

4. A general discussion of catalytic reactions has shown why the three so-called laws of catalysis given above were deduced from the experimental material, and under what conditions they do or do not hold in catalytic reactions.

JOHNS HOPKINS UNIVERSITY,
May 1, 1907.

¹ Acree and Hinkins: *THIS JOURNAL*, **28**, 370.

CXLV.—NOTE ON THE SYNTHESIS OF IODGORGIC ACID.

By HENRY L. WHEELER.

In 1905 the writer, with Dr. G. S. Jamieson, described the synthesis of iodorgic acid¹ and showed that this substance, previously obtained only from gorgonin,² the axial skeleton of the Mediterranean coral *Gorgonia Cavolini*, was diiodtyrosin.

Believing at that time we were dealing with *l*-tyrosin, having prepared it from silk, horn and casein (see below), we stated "that a diiodtyrosin, having all the properties of iodorgic acid, can be prepared by adding a little less than the calculated amount of iodine to a solution of *l*-tyrosin in two molecular proportions of potassium or sodium hydroxide, at ordinary temperatures."

It now develops that Henze,³ following our directions and using *l*-tyrosin, has succeeded in preparing a diiodtyrosin which he very positively states is not identical with iodorgic acid. He found, however, if our method is followed, using inactive tyrosin instead of the *l*-modification, that the product then obtained is identical in every respect with the natural iodorgic acid.

Henze's conclusion that the synthetic diiodtyrosin and the natural iodorgic acid are identical is a gratifying confirmation of the correctness of our previously published views; but Henze makes it appear that we were dealing with his *l*-diiodtyrosin, in spite of the fact that the properties of our diiodtyrosin do not agree with those of this substance. If it was true that our product was *l*-diiodtyrosin then we could not have had iodorgic acid.

We wish now to have it positively understood that Henze's *l*-diiodtyrosin is certainly not identical with the product obtained by us and which we described as iodorgic acid.

¹ THIS JOURNAL, **33**, 365 (1905).

² Drechsel: Zeit. f. Biologie, **33**, 90 (1896).

³ Z. physiol. Chem., **51**, 64 (1907).

It is now obvious that our tyrosin had been rendered inactive by the treatment which it received in its preparation, and that our synthetic iodogorgoic acid was inactive diiodtyrosin. Emil Fischer states in regard to tyrosin obtained by the cleavage of proteins by acids: "Ich halte es aber auch für möglich, dass dem Tyrosin welches aus Eiweisskörpern durch Spaltung mit starker Salzsäure* * * * gewonnen ist, eine wechselnde Menge racemischer Base beigemischt ist."¹ Henze's *l*-diiodtyrosin liberates iodine on warming with water. He says it often happened that it completely decomposed when an attempt was made to dissolve it in hot water.

It seems to us that it would be clear to any one that we should not claim such a substance as this, which decomposes on boiling with water, to be identical with a product that is obtained by prolonged boiling of protein with barium hydroxide. In our paper, page 369, we stated that the synthetic iodogorgoic acid "can be repeatedly crystallized from water without change." We found that it could be boiled (2 hours) with a strong solution of barium hydroxide without any iodine being removed; after about 30 hours only 10 per cent of the iodine was liberated. Finally, we mentioned a sealed tube experiment to illustrate its stability: "One-half gram was heated in a closed tube, with 5 cc. of water, for 2 hours, at 120°-130°; only a partial decomposition took place."

Knowing the properties of the true *l*-diiodtyrosin, and with these facts at hand, Henze, nevertheless, misrepresents us by continually referring to our product as *l*-diiodtyrosin.

Henze gives a characteristic test for *l*-diiodtyrosin. This is that if *l*-diiodtyrosin is boiled with dilute alcohol a peculiar swelling (Aufquellen) of the crystals is observed. If the boiling is continued with careful addition of water there is obtained, finally, a light yellow solution (iodine) which, on cooling, gives a transparent jelly.

A specimen of our synthetic iodogorgoic acid was found which had been left over from our work. This was treated as described in the above test, whereupon, it was found that the crystals did not swell up, although examined under the micro-

¹ Ber. d. chem. Ges., 32, 3643 (1899).

scope; that no jelly was formed, but instead the material finally dissolved and crystallized out again on cooling unaltered. According to Henze's own test, therefore, the substance was not *l*-diiodtyrosin.

In our previous work we examined our synthetic iodorgoic acid in regard to its behavior towards polarized light, and we found that it was inactive. The amount of material examined was small and, therefore, no mention was made of this observation.

We prepared our tyrosin for use from silk, horn and casein by prolonged boiling with sulphuric acid, 1 part acid : 5 of water. The sulphuric acid was removed from the hot solution by an excess of lime, considerable heat being generated by this treatment, and the excess of lime was precipitated from the hot solution by means of carbon dioxide. On evaporation, the tyrosin that separated was purified in the usual manner.

Finally, it may be said that the best reaction to identify iodorgoic acid is, as we have shown, its ready conversion into tyrosin by warming with concentrated hydriodic acid.

NEW HAVEN, CONN.,
April, 1907.

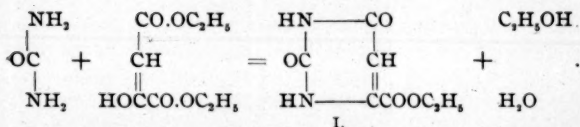
CXLVI.—RESEARCHES ON PYRIMIDINES: URACIL-4-CARBOXYLIC ACID.

[TWENTY-THIRD PAPER.]

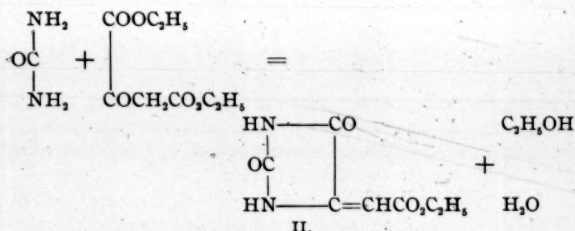
BY HENRY L. WHEELER.

In 1897, Müller¹ described a substance obtained by condensing oxalaceticethyl ester with urea by means of hydrogen chloride in glacial acetic acid. His analytical results showed that the condensation involved the separation of water and alcohol, and he represented the reaction as taking place with the formation of uracil-4-ethylcarboxylate as follows:

¹ J. prakt. Chem., 56, 488 (1897).

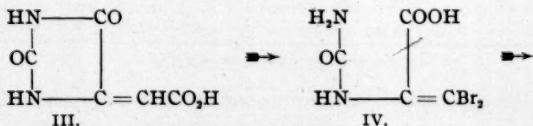


There is nothing in Müller's article, however, to show that the product formed was a pyrimidine. The condensation might result with the separation of water and alcohol from the oxalyl radical; the process would then be represented as follows:

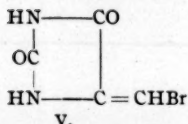


An acid called pyvureidic acid (Pyvureidsäure), corresponding to this ester, has been recently described by Gabriel,¹ who obtained it by treating malyureidic acid with bromine.

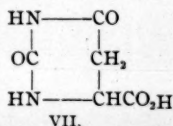
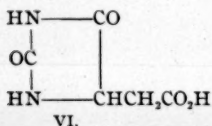
Formula III. has been assigned by Gabriel to pyvureidic acid since with bromine water it yields dibrompyvurinic acid, IV., the same substance also being obtained in a similar manner from brompyvureid, V.



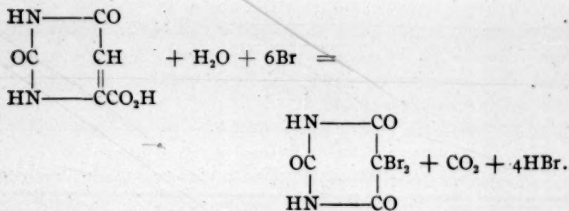
¹ Ann. Chem. (Liebig), 348, 89 (1906).



Since pyvureidic acid is to be represented by formula III., then malyureidic acid has the five-membered ring structure, VI., given to it by Guareschi¹ and not that of a dihydrouracil-carboxylic acid, VII., as represented by Grimaux.²



The writer has prepared Müller's ester and finds, on saponification, that it gives an acid isomeric, and not identical, with Gabriel's pyvureidic acid. The action of bromine water on this acid shows that the substance is a pyrimidine. This was tried, following the directions given by Gabriel in the case of pyvureidic acid. The acid dissolved, carbon dioxide was evolved and, on evaporating the solution, large crystals of dibrombarbituric acid separated. The reaction can be represented as follows:



This proves that the acid in question is uracil-4-carboxylic

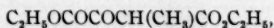
¹ Ber. d. chem. Ges., 10, 1748 (1877).

² Jahres. d. Chem., 1876, p. 752. Ann. chim. phys. [5], 11, 413 (1877). Bull. Soc. Chim. [2], 24, 337 (1875).

acid and that Müller's ester has the pyrimidine structure, I., originally assigned to it. It also confirms Gabriel's conclusions that pyvureidic and malyvureidic acids are not pyrimidines.

Uracil-4-carboxylic acid has its carboxyl group much more firmly bound than the isomeric uracil-5-carboxylic acid. It is not converted into uracil when heated with 20 per cent sulphuric acid at 200°, while the isomeric 5-derivative readily yields uracil on heating with acids.¹ This excludes the possibility that uracil exists in the nucleic acids as a 4-carboxyl derivative. Unlike the isomeric pyvureidic acid, uracil-4-carboxylic acid crystallizes with 1 molecule of water of crystallization. The hydrous acid has the empirical formula of orotic acid, but its melting point is different. The melting point of its methyl and ethyl esters also differ from those of the corresponding esters of orotic acid.

The yield of uracil-4-ethylcarboxylate, by Müller's method, is only about 20 per cent of the calculated, and attempts were made to prepare it by treating ethylpseudothiourea hydrobromide in alkaline solution with oxalaceticethyl ester. This gave no pyrimidine, but instead a pseudourea addition product or salt. Owing to the poor yield of this product, no attempt was made to convert it into the pyrimidine by heating, as has been found to prove successful by Gabriel and Colman in the case of the analogous addition product of anisamidine and acetylacetone.² In this connection, and in regard to the limits of our general method for the preparation of pyrimidines, it is interesting to note that such acid molecules as acetylcyanacetate, $\text{CH}_3\text{COCH}(\text{CN})\text{CO}_2\text{C}_2\text{H}_5$, and oxal-malonic ethyl ester, $\text{C}_2\text{H}_5\text{OCOC}\text{OCH}(\text{CO}_2\text{C}_2\text{H}_5)_2$, also failed to condense with the pseudourea, but like oxalacetic ethyl ester, formed addition products. On the other hand, Dr. Johnson has found that oxalpropionic ester,



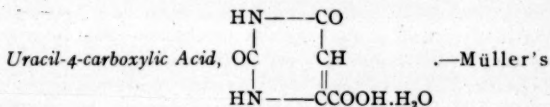
condenses normally in alkaline solution, giving 2-mercapto-4-carbethoxy-5-methyl-6-oxypyrimidine.

¹ *THIS JOURNAL*, **37**, 392 (1907).

² *Ber. d. chem. Ges.*, **32**, 1529 (1899).

Ruhemann and Stapleton¹ found that ethyl acetylenedicarboxylate, $C_2H_5OCOC\equiv CCOOC_2H_5$, condenses with guanidine to form 2-amino-6-oxy-4-ethylcarboxylate; whether uracil-4-carboxylic acid can be prepared more readily from this substance than by the above method, or, by the condensation of the acetylene ester with a urea derivative, must be left for future work to decide.

EXPERIMENTAL PART.



"Uracilcarbonsäureäthylester" was prepared according to his directions.² It was found that 18 grams of oxalacetic ethyl ester, after 2 weeks, gave a little over 4 grams of uracil-4-ethylcarboxylate and that 60 grams of oxalacetic ethyl ester gave about 12 grams of the crude pyrimidine.

The ester was saponified as follows: Five grams were dissolved in about 60 cc. of hot alcohol and twice the calculated amount of potassium hydroxide (3 grams) in 10 cc. of water, was added; the whole then solidified to a thick mass. A clear solution was obtained by adding about 150 cc. of water. This was then evaporated to a small volume and the acid was precipitated by adding dilute hydrochloric acid in excess. The yield was near the calculated. The acid is very difficultly soluble in alcohol. It was purified for analysis by crystallizing from water. It is moderately soluble in hot water, difficultly soluble in cold, and it separates in the form of microscopic, stout, twinned prisms, some in the form of a cross.

0.6929 gram substance lost 0.0712 gram of water when heated 1 hour at 125°-130°.

	Calculated for $C_5H_4O_4N_2 \cdot H_2O$.	Found.
H_2O	10.34	10.26
N	16.09	16.12

¹ J. Chem. Soc. Proc., 18, 121 (1900).

² J. prakt. Chem., 66, 488 (1897).

The acid usually melts at 347° with strong effervescence; occasionally samples were obtained which decomposed on heating without effervescence. It gives a white, amorphous precipitate with silver nitrate, soluble in nitric acid. The aqueous solution gives a crystalline precipitate with barium chloride. When heated (0.5 gram) with 20 per cent sulphuric acid (5 cc.) at 185° – 208° , for 2 hours, no uracil was formed. A portion of the solution was tested with bromine water and barium hydroxide¹ for uracil, but no color whatever was obtained. Therefore, there could not have been as much as 0.005 gram of uracil formed. The material remaining was crystallized from water, whereupon it melted at 347° with vigorous effervescence.

It was found that the acid (0.5 gram) was not attacked by fuming nitric acid (10 cc.) when boiled and then evaporated to dryness on the water-bath. The operation was repeated with 20 cc. of fuming nitric acid. There sidue then, when crystallized from water, melted with effervescence at 347° . This experiment shows that in the preparation of nitrouracilcarboxylic acid,² by nitrating 4-methyluracil, it is the 5-position that is first attacked.

Action of Bromine Water: Dibrombarbituric Acid.—Three grams of the above acid were suspended in 20 cc. of water and 6 grams of bromine added. Carbon dioxide was given off, and the acid slowly dissolved when more bromine was added. The solution was evaporated in a flat dish at about 50° . It then deposited long, colorless, flat, narrow prisms; one that separated was 2.5 inches in length.

	Calculated for $C_4H_2O_3N_2Br_2$.	I.	Found. II.	III.
N	9.79	10.04	9.87	..
Br	55.94	..	..	56.49

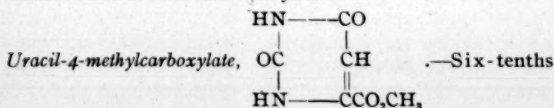
This material was compared with some dibrombarbituric acid, prepared by treating barbituric acid with bromine and water, as above. Similar crystals were obtained. Both preparations had the following properties: they melted,

¹ J. Biol. Chem., **3**, 1907.

² Behrend: Ann. Chem. (Liebig), **229**, 36 (1885).

when heated under the same conditions, with effervescence, at 235° , and the melting or decomposing point was not altered when the two were mixed. Ammonium or barium hydroxide gave no color.

When hydrogen sulphide was passed into the aqueous solution sulphur separated, and then, on boiling off the excess of hydrogen sulphide and adding barium hydroxide, a purple or violet-blue precipitate was formed. Baeyer¹ has shown that dibrombarbituric acid gives dialuric acid when treated with hydrogen sulphide, and dialuric acid gives a violet-blue precipitate with barium hydroxide, as observed by Behrend and Roosen.² The samples in alcohol gave precipitates having the same appearance when mixed with alcoholic solutions of thiourea and ammonium thiocyanate.



of a gram of uracil-4-carboxylic acid was suspended in 100 cc. of methyl alcohol and saturated with hydrogen chloride. After warming a day the acid dissolved, and on cooling a mass of colorless needles separated. This ester formed needles or prisms from water and it melted to an oil at 230° .

	Calculated for $\text{C}_5\text{H}_6\text{O}_4\text{N}_2$	Found.
N	16.47	16.45

The Potassium Salt, $\text{C}_5\text{H}_3\text{O}_4\text{N}_2\text{K}$.—This normal salt was formed when the acid and potassium hydroxide, in molecular proportions, were mixed in aqueous solution. Uracil-5-carboxylic acid, under these conditions, gives an acid salt. It separated on cooling the aqueous solution as a felt-like mass of fine, colorless needles. It showed no signs of melting at 355° .

	Calculated for $\text{C}_5\text{H}_3\text{O}_4\text{N}_2\text{K}$.	I.	Found.	II.
N	14.43	14.23		14.17

¹ Ann. Chem. (Liebig), **130**, 133 (1864)

² *Ibid.*, **351**, 244 (1889).

The Barium Salt, $(C_5H_3O_4N_2)_2Ba$.—This salt separates in the form of needles or prisms when hot aqueous solutions of the acid and barium chloride are mixed.

	Calculated for $C_{10}H_6O_8N_4Ba$.	I.	Found.	II.
N	12.51	12.12		12.20

Oxalaceticethyl Ester and Ethylpseudothiourea Hydrobromide.—Fifty grams of Kahlbaum's oxalaceticethyl ester, 50 grams of the ethyl bromide addition product of thiourea, and 22 grams of sodium hydroxide, in a little over 100 cc. of cold water, were mixed and allowed to stand over night. The next day about 10 grams of crystalline material had separated. This was found to be difficultly soluble in water and readily soluble in hot alcohol. When crystallized from a mixture of equal volumes of alcohol and water it formed balls of colorless needles, which melted to a clear oil at 133° – 134° . The analytical results and the behavior of the substance agreed with the view that this substance is an addition product.

	Calculated for $C_{11}H_{10}O_3N_2S$.	I.	Found.	III.
N	9.58	9.33	9.43	9.32

When this substance was boiled with hydrochloric or hydrobromic acid it gave a product which melted at 206° – 207° . This was very soluble in alcohol. From water it separated in the form of needles or prisms. It contained sulphur, but no nitrogen, and since it was not a pyrimidine it was not further examined. The alkaline solution from which the addition product had separated was acidified with hydrochloric acid; a small amount of oil separated but no mercaptopyrimidine.

Acetyethylcyanacetate and Ethylpseudothiourea Hydrobromide.—Fifteen grams of acetyethylcyanacetate, prepared by Haller's method,¹ were mixed with 18 grams of the ethyl bromide addition product of thiourea in 18 cc. of water and then 12 grams of potassium hydroxide in a little cold water added. This produced a white precipitate, which, after stand-

¹ Ann. Chim. Phys. [6], 17, 207 (1889).

ing over night, weighed 8.4 grams. When this was crystallized from alcohol it gave colorless, twinned, flat prisms, having the form of the letters *x* and *y*. They melted at 159° , with effervescence, and were found to be free from ash. The analytical results agreed with the calculated for an addition product of equal molecules of the pseudourea and acetylcyanacetate. Acids produced no precipitate in the alkaline filtrate from this material.

N	Calculated for $C_{10}H_{17}O_5N_2S$.	I.	Found.	II.
	16.21	16.23		15.86

When boiled with alkali, acids or acetic anhydride, the substance decomposed.

Oxalmalonic Ethyl Ester¹ and Ethylpseudothiourea Hydrobromide.—These substances were mixed with potassium hydroxide in molecular proportions in aqueous solution. On standing over night, crystals separated; they were very soluble in hot water and somewhat less so in alcohol, from which solvent the material crystallized in the form of shining scales, which melted, with effervescence, at 181° . This material gave analytical results agreeing with the calculated for an addition product of 2 molecules of the pseudourea to 1 molecule of oxalmalonic ethyl ester.

N	Calculated for $C_{17}H_{26}O_7N_4S_2$.	I.	Found.	II.
	11.96	11.95		12.08

When two molecular proportions of potassium hydroxide were used, a granular potassium salt separated which was free from sulphur.

NEW HAVEN, CONN.,
May, 1907.

¹ Bouveault: Bull. Soc. Chim. [3], 19, 78 (1898).

From the Chemical Laboratory, Bureau of Science, Manila, P. I.

THE ACTION OF SODIUM ON ACETONE.

BY RAYMOND FOSS BACON AND PAUL C. FREER.

A number of years ago one of us¹ described the action of sodium on acetone, showing that in the presence of absolute ether a *white* sodium derivative is obtained which contains 30.17 per cent of sodium (calculated for sodium acetone 28.75 per cent) and which, on being added to dilute hydrochloric acid, regenerates acetone. Subsequently,² in a second discussion of the subject, it was demonstrated that hydrogen is evolved when sodium acts on acetone, and the resulting sodium derivative was again described as being *white*, but *turning red* rapidly on exposure to air and moisture. It was also shown that when this sodium derivative is added to dilute hydrochloric acid and *repeatedly extracted with ether*, no condensation products of acetone, or at least only traces, could be isolated. The sodium derivative, therefore, does not contain these condensation products to any great extent. The mother liquors from a number of preparations of sodium acetone were carefully retained, united, washed with water, extracted with ether and the residue distilled, a very small quantity of mesityl oxide and some higher condensation products of acetone being isolated. Again, in another discussion of the subject,³ by treating sodium, under xylene, with acetone, 62.7 per cent of the theoretical amount of hydrogen was obtained, an observation which was subsequently confirmed by Beckmann and Schliebs.⁴ In the same paper, in discussing the preparation and analysis of the sodium derivative of acetone, it was shown that delay during the preparation of this derivative always resulted in increasing the percentage of sodium. A large number of samples of acetone-sodium were prepared, decomposed by dilute, ice-cold acetic acid, and united until a sufficient amount was collected to study

¹ THIS JOURNAL, 12, 355 (1890).

² *Ibid.*, 13, 320 (1891).

³ *Ibid.*, 15, 585 (1893). Ann. Chem. (Liebig), 278, 116.

⁴ *Ibid.*, 289, 86 (1896).

the reaction products; acetone, isolated as the sodium bisulphite compound, isopropyl and ethyl alcohols were identified among these. Under favorable circumstances fully twice as much acetone as isopropyl alcohol was isolated. The high-boiling fractions from the separation of the above substances, gave pinacone, a small quantity of phorone and, presumably, reduction products of the latter. Mesityl oxide *could not be isolated*. A portion of the reaction product of sodium on acetone was found to be soluble in ether; this, on careful evaporation, gave a *yellow powder*,¹ which oxidized in the air with remarkable readiness. When this residue was acidified an oil separated, which was isolated, and the presence of acetone was afterward proved in the solution. The high-boiling portion of the residue was phorone. These high-boiling oils *react readily with phenylhydrazine*. No isopropyl alcohol and but very little pinacone can be found among the products of decomposition of this soluble portion obtained by the action of sodium on acetone, but by far the greater part of the condensation products produced by the action of sodium on acetone are found in this residue. In proportion as such condensation products are produced, the percentage of sodium in sodium acetone will be increased.

Recently,² Millicent Taylor has returned to the subject and comes to the remarkable conclusion that acetone-sodium "consists chiefly of caustic soda mixed with a small proportion of the sodium derivatives of alcoholic reduction and condensation products of acetone."

Apart from the fact that in her discussion Miss Taylor completely ignored the careful description given by one of us of all of the products obtained by the action of sodium on acetone, the statement made by her that "so-called sodium acetone" contains 50.4 per cent of sodium would, in itself, be sufficient to raise a doubt as to the accuracy of her results. In our opinion the fact that the product of the action of sodium on acetone, after all acetone and solvent has been removed, *regenerates acetone in large amount* when acidified, is conclusive evidence of the existence of sodium

¹ Our work shows that, under proper conditions, this residue is white.

² J. Chem. Soc., 89, 1258 (1906).

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07

acetone, and this fact was repeatedly emphasized in the first series of papers on this subject, but ignored by Miss Taylor in her discussion. Nevertheless, we have deemed it necessary to repeat the work, and here it may be said that at no time, even with the absence of all of the usual precautions, were we able to find as much as 50 per cent sodium in the derivative of the action of sodium on acetone; in ether we obtained 29.2–30.9 per cent of sodium, and the highest determination, in petroleum ether, gave us 35.5 per cent, these results being in accord with those previously obtained by one of us. In carefully reading Miss Taylor's paper it becomes evident that she always had a *red* substance present after the action of sodium on acetone, both in her experiments on the determination of the amount of sodium in the insoluble precipitate and in the soluble portion. It has in the past been expressly stated that sodium acetone, when prepared with all precautions, is *white* and that reddening is due to decomposition in the air or by reason of moisture.

EXPERIMENTAL.

Sodium acetone is a very sensitive substance. When properly prepared and when air and moisture are rigidly excluded it is a *snow-white*, flocculent solid. On exposure to the air and to moisture it becomes pink, then red and brown, an oil at the same time separating; the color changes represent the formation of sodium hydroxide and condensation products of acetone. Of course, as had previously been shown, sodium acetone also contains sodium isopropylate, some sodium pinaconate and, in the reactions performed under ether, some sodium ethylate. All ether which we used in these experiments was repeatedly dried and distilled from sodium wire until this wire remained perfectly bright under the solvent. The acetone was from the bisulphite compound and was dried four times over phosphorus pentoxide, each time being poured off and distilled. Dry hydrogen was run through the acetone for some hours to remove any air or carbon dioxide and it was then kept over fused sodium sulphate and protected from moisture and carbon dioxide by tubes containing phosphorus pentoxide and soda lime.

Experiment 1.—The apparatus used was that described by Freer.¹ About 1.6 grams of sodium, cut under coal oil and then washed with absolute ether, were rapidly squeezed as a very fine wire into about 50 cc. of absolute ether in the reaction flask, and the apparatus quickly closed. Dry and pure hydrogen was now run through the apparatus for 3 hours. The reaction flask was then surrounded by ice and 10 cc. of acetone dissolved in 50 cc. of absolute ether, gradually added through a dropping funnel. Bubbles of hydrogen were given off and the separation of a white, gelatinous precipitate soon commenced. When all of the sodium had disappeared, the ether and precipitate were sucked into a filtering tube, the latter washed eight times with absolute ether, using 50 cc. each time and always sucking as dry as possible. The precipitate was then dried to constant weight in a current of hydrogen, weighed, and decomposed with dilute, ice-cold sulphuric acid. Only a minute amount of acetone condensation products was obtained, as the sodium salt was practically completely soluble in water. In no instance, if the sodium derivative had been properly prepared, was there more than a drop or two of insoluble oil. When small amounts of air or moisture gain access to the sodium derivative, or when the decomposition by acids is not carefully conducted, then these condensation products result, the greater the decomposition the greater their amount.

There were obtained 2.65 grams of pure, white sodium acetone, containing 0.8052 gram sodium.

	Required for C_3H_5ONa .	Found.
Na	28.75	30.3

The acid solution resulting from the decomposition of the product of the action of sodium on acetone was now rendered alkaline with ammonia and iodine, dissolved in ammonium iodide, added until the color of iodine no longer disappeared. There resulted 6.5 grams of iodoform, equal to 1.0 gram acetone, or 53 per cent of the amount calculated for pure sodium ace-

¹ THIS JOURNAL, 15, 588 (1893).

tone.¹ Undoubtedly, some loss of iodoform occurs in evaporating its ethereal solution, and all acetone is not converted into iodoform, so that the percentage of acetone is probably really higher than given above.

Experiment 2.—About 1.5 grams of sodium wire were dissolved in an excess of acetone diluted with absolute ether, the whole being in an Ehrlenmeyer flask having a very small neck. The flask was not surrounded by ice, the heat generated by the reaction evidently volatilizing enough ether to exclude air; the sodium derivative remained white. The sodium compound was now rapidly filtered on a Hirsch funnel by means of a strong suction, quickly washed six times with ether and then dried in a vacuum desiccator over sulphuric acid and paraffin. The salt was somewhat pink but as soon as it was dry it was weighed to 0.1 gram as quickly as possible and then thrown into ice-cold, dilute acid. The acid was now saturated with potassium carbonate and the low-boiling portion distilled on a water-bath. The distillate was saturated with a solution of sodium bisulphite and the whole cooled in ice for an hour. The acetone-sodium bisulphite (4.5 grams from 3.8 grams of sodium compound) was filtered and decomposed with sodium carbonate, the acetone being distilled. There resulted 1 gram of acetone boiling at 54°–57°.

Experiment 3.—This was carried out the same as Experiment 2, with the difference that a sodium determination was made by using an excess of standard acid (found 30.9 per cent). This experiment gave 4.2 grams of iodoform, corresponding to somewhat less than one-half the theoretical yield of acetone for pure sodium acetone.

As will be seen, even in the above two experiments, when air was not rigidly excluded and where the sodium derivative was not handled with particular care, no such high percentage

¹ We have once more tested this method of determining acetone in the presence of isopropyl or ethyl alcohol, and can confirm the former statements of Freer that it is sufficiently accurate for the work in hand, the results being *under* rather than over the amount of acetone. Dinger's very convenient method of determining acetone is unsuitable, as both isopropyl alcohol and mesityl oxide give precipitates with his reagent. Denigès: *Compt. rend.*, 127, 963 (1898); *Ann. Chim. Phys.*, 18, 400 (1899); *Bull. Soc. Chim.*, 3, 31, 241 (1899). Oppenheimer: *Ber. d. chem. Ges.*, 32, 986 (1899); *Centrabl.* II, 888 (1899).

of sodium as that obtained by Miss Taylor was found. Indeed, in a long series of experiments we have never been able to obtain her results, which can only be accounted for by a deep decomposition of her sodium derivative and the washing out of the acetone condensation products which would be formed. If this decomposition were allowed to go far enough, then practically nothing but sodium hydroxide mixed with the sodium derivatives of alcoholic reduction products, would remain.

Experiment 4.—This was performed as was Experiment 1, with the exception that petroleum ether was substituted as a solvent. The reaction in this case is not so clean cut as with ether; the resulting compound is somewhat pink and the sodium percentage higher.

1.745 grams of the sodium derivative gave 0.6203 gram of sodium and 3.4 grams of iodoform, equivalent to 35.5 per cent of sodium and 0.52 gram of acetone equivalent to 41.0 per cent, respectively.

Experiment 5.—The apparatus was the same as in Experiment 1. The sodium compound, as obtained, weighed 8.515 grams and gave 2.567 grams of sodium, equivalent to 30.14 per cent. After the sodium salt had been decomposed the acid solution was divided into 4 parts. One of these was saturated with sodium acetate, then made very slightly alkaline and the theoretical quantity of semicarbazide hydrochloride was added. A precipitate of crystalline needles rapidly formed. This mixture after standing for 12 hours in the ice chest was filtered and gave 1.2 grams of acetone semicarbazone, m. p. 186° . This was identical in all respects with a specimen of the same body prepared for comparative purposes. One-eighth of the original acidified solution gave 1.3 grams of iodoform.

Experiment 6.—The conditions were the same as in Experiment 1. Eight and twenty-five one-hundredths grams of sodium derivative were obtained; from one-half of this, acidified, etc., 2.9 grams of acetone semicarbazone, m. p. 186° , were separated; from one-quarter 2.2 grams of iodoform

were precipitated. One other sodium determination gave us 29.2 per cent of sodium.

The above experiments render it practically certain that a sodium derivative of acetone exists among the products of the action of sodium on acetone, as acetone is obtained by their decomposition with acids. However, it might possibly be true that the reaction product is sodium isopropylate together with some sodium hydroxide and that the acetone which is found is held by the sodium isopropylate in a combination somewhat similar to alcohol of crystallization. That this is unlikely is proved by the fact that the sodium derivative formed by the action of sodium on acetone, after filtering and washing, was dried *in vacuo* to constant weight, while at the same time it was *warmed* until decomposition began. If acetone was present in a condition such as the above, it certainly would be driven off by this treatment; nevertheless, the sodium derivative behaved as usual when it was added to dilute acid. That sodium isopropylate does not behave like sodium acetone, even when it is mixed with acetone, is shown by the following:

Experiment 7.—Two and five-tenths grams of sodium were dissolved in an excess of isopropyl alcohol and diluted with absolute ether. The white color did not change in the least when the derivative was allowed to stand for three hours in an open beaker, whereas the product of the action of sodium on acetone, placed beside it under the same conditions, decomposed and completely changed in five minutes. When acetone was added to sodium isopropylate under ether, the resulting mixture remained unchanged for a long time when exposed to the air, although after one hour it had assumed a slightly pink tinge. It was now filtered, washed three times with absolute ether, dried and thrown into dilute sulphuric acid. The usual acetone test gave no trace of iodoform. Acetone is, therefore, not retained by sodium isopropylate.

Miss Taylor suggests that the reaction first observed by one of us may be due to the formation of the sodium salt of diacetone alcohol, $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{COCH}_3$. This compound is formed from acetone in the cold, under the influence of hy-

droxyl ions. Koelichen¹ has shown that in the presence of hydroxyl ions there is an equilibrium between the amounts of acetone and of diacetone alcohol; thus, with a concentration of hydroxyl ions represented by a 10 per cent solution of sodium hydroxide, the quantity of diacetone alcohol is 3 per cent of the total acetone, and smaller in quantity for a lower concentration of the ions. The sodium compound of this body would contain 14.73 per cent of sodium. We have prepared diacetone alcohol according to the method of Koelichen and subjected it to the action of sodium. The alcohol was diluted with absolute ether and in an open beaker dissolved sodium very rapidly, with marked reddening of the resulting compound, the action resembling closely that observed when acetone is similarly treated in the open air, but on acidifying the product, mesityl oxide and other condensation products of acetone are separated, and the presence of acetone could be demonstrated in the solution by the formation of its semicarbazone, m. p. 185°-186°.

A different result is obtained in an atmosphere of dry hydrogen. In the apparatus used in Experiment 1, and under absolute ether, diacetone alcohol is only very slowly attacked by sodium, giving a yellowish sodium derivative. Over four hours were consumed in dissolving 0.5 gram of sodium in 5.5 grams of the alcohol. The precipitate was filtered, dried in a current of hydrogen and dissolved in dilute acid, a considerable quantity of condensation products of acetone separating. Seventy-four hundredths gram of the sodium derivative gave 1.067 grams of sodium sulphate or 46.8 per cent of sodium. It seems evident, therefore, that sodium acting on diacetone alcohol really does give sodium hydroxide and the condensation products of acetone; the reaction is, however, so radically different from the action of sodium on acetone, and the condensation products so prominent, whereas there are scarcely any when pure sodium acetone is dissolved in dilute acids, that the theory that diacetone alcohol is first formed, subsequently to be acted on by sodium, must be abandoned. There remains only the question, then, whether sodium acetone

¹ *Z. physik. Chem.*, **23**, 129 (1900). *Heintz: Ann. Chem. (Liebig)*, **169**, 114 (1873).

may not react with acetone to give the sodium derivative of diacetone alcohol, although in this event the percentage of sodium found should be very much less than it really is. However, apart from this, in the absence of condensation products of acetone on acidifying, it must be presumed, to account for the acetone which is always found in the acidified solutions of sodium acetone, that the diacetone alcohol would promptly be reconverted into acetone during this process. Rigidly, to exclude this supposition, we performed the following experiment:

Experiment 8.—Four grams of diacetone alcohol were dissolved in 20 cc. of ethyl alcohol and 20 cc. of water. The solution was saturated with sodium acetate and 4 grams of semicarbazid hydrochloride were added. The solution was then rendered very faintly alkaline and placed in ice-water for 1 hour, being vigorously scratched with a glass rod. No precipitate appeared. To be sure that the conditions were correct for the formation of a semicarbazone, the solution was divided into two equal portions. To the second portion 2 grams of acetone were added, whereupon a precipitate of crystalline needles immediately appeared. Four grams of semicarbazide hydrochloride were now added to this portion of the original solution, so that enough of the reagent should be present to precipitate all acetone and all diacetone alcohol, should it form a semicarbazone. Both the original, unchanged portion and the second one were kept in the ice-chest over night. In the morning, the first portion, to which no acetone had been added, contained a very faint precipitate of acetone semicarbazone, 0.01 gram, m. p. 185° – 186° , so that a very small amount of acetone had been separated by hydrolysis. From the second portion, 2.5 grams of acetone semicarbazone were isolated, m. p. 186° .

From the above result it is evident that the acetone semicarbazone obtained in the preceding experiments could not have originated in the sodium derivative of diacetone alcohol, as the hydrolysis of the latter body proceeds slowly.

The above results confirm the previous work in every way

and establish the fact that the action of sodium on acetone gives a sodium derivative which can only be sodium acetone.

In view of these conclusions it is not deemed necessary further to discuss Miss Taylor's work because, apparently, she had not reproduced the conditions under which Freer worked. A very short review of some of the chief facts established in the earlier literature, and which Miss Taylor appears not to have considered, may not be out of place, as it will serve to recall some of the arguments which were not discussed in Miss Taylor's paper. The portion of the product of the action of sodium on acetone, which is insoluble in ether, was shown by Freer¹ to consist of acetone sodium, sodium isopropylate and disodium pinaconate, the soluble portion of a sodium derivative of acetone; no sodium isopropylate was isolated from this soluble portion and, if it is not carefully acidified, mesityl oxide and phorone are also obtained. In studying the products of the action of ethyl chlorcarbonate on sodium acetone, Miss Taylor suggests that a mixture of ethyl isopropylcarbonate and diethyl carbonate would yield 34 per cent of carbon dioxide, whereas Freer found 33.89 per cent on decomposing the oil boiling at 128°–129° and produced by the interaction of sodium acetone and ethyl chlorcarbonate—calculated CO_2 for $\text{CH}_3\text{C}(\text{OCO}_2\text{C}_2\text{H}_5):\text{CH}_3$, 33.84 per cent; but Miss Taylor appears to have overlooked the statement² that Freer also proved the presence of ethyl alcohol and acetone in the products left after saponification. If acetone had been present as mesityl oxide, the percentage of carbon dioxide would have fallen very much. It was further shown by Freer that the fraction boiling at 128°³ yielded, on decomposition with dilute acid, a sufficient amount of acetone to allow of its being separated as the acetone sodium bisulphite compound. Found: carbon dioxide, 33.7 per cent. The quantity of ethyl alcohol was less than one-half the organic liquid isolated; it boiled at 78°. We should therefore, if we were dealing with a mixture of diethyl carbonate, ethyl isopropyl carbonate and mesityl oxide, need to assume a large proportion of the latter sub-

¹ THIS JOURNAL, 18, 592 (1893).

² *Ibid.*, 13, 325 (1891).

³ *Ibid.*, 17, 11 (1895).

stance to be present, and this would inevitably have lowered the carbon dioxide very markedly. Furthermore, the oil boiling between 132° and 137° yielded 30 per cent of acetone (calculated, 48.8 per cent) and this figure, because of the difficulties in quantitative estimation, is undoubtedly too low. It does not seem reasonable to assume that an oil which would contain a sufficient quantity of mesityl oxide to yield so much acetone would not further react with phenylhydrazine; but, on the other hand, this percentage would correspond to a total of 62 per cent of the isoacetone ester in the oil. Miss Taylor's supposition is that this acetone comes from mesityl oxide present in the mixture. If enough mesityl oxide occurred in the mixture to yield 30 per cent of acetone, then the carbon dioxide found would be reduced 11 per cent, to say nothing of the change brought about in the analytical results. A mixture which consists of ethyl isopropyl carbonate, diethyl carbonate and sufficient mesityl oxide to yield 30 per cent of acetone, and which will also give 33.7 per cent of carbon dioxide, cannot be calculated. Miss Taylor allowed her reaction product to stand over phenylhydrazine for four days. It is possible that, if ethyl isopropenyl carbonate was present at all, it would by that time have reacted with phenylhydrazine; it is also possible that, owing to some variation in her work, Miss Taylor never had the substance in the oil she prepared. Attention is further called to the fact that Freer obtained enough 2-chlorpropene, by the action of phosphorus pentachloride, to isolate this very low-boiling substance. The reaction product also absorbs bromine in the cold, without yielding hydrobromic acid.

Miss Taylor did not use benzoyl chloride in studying the composition of sodium acetone, substituting *p*-nitrobenzoyl chloride therefor. Again, in her reaction she does not seem to have had a sodium derivative which acted like the one described above, for she obtained *none of the addition* products described by Freer as a result of the action of benzoyl chloride on sodium acetone. That *p*-nitrobenzoyl chloride might not form an isoacetone ester is conceivable, but in that event it *should* give addition products. Freer, in studying the action

of benzoyl chloride on sodium acetone, separated the reaction products into 2 parts, one soluble in alkalis, the other insoluble. In this instance, the insoluble oil, 12 grams, boiling at 120° (39 mm.) added bromine in the cold, gave acetone in sufficient quantity to be isolated from the sodium bisulphite compound, isopropyl alcohol and ethyl alcohol. The liquid containing the acetone was twice as great in volume as the remainder. The portion of the reaction product which was soluble in alkalis yielded acetophenone, *mono-* and *dibenzoyl* acetone. Here we are not dealing with a mixture of oils, but with crystalline solids which can be isolated in the pure state. It is difficult to see how *mono-* and *dibenzoyl* acetone could result from a mixture of condensation products of acetone, sodium isopropylate and sodium hydroxide. Sodium acetone must have taken part in the reaction.

It should also be remembered that Freer and Lachman,¹ in studying the action of sodium on methyl propyl ketone, obtained 22.1 per cent of sodium in the derivative; calculated 21.3 per cent, isolated dibenzoyl methyl propyl ketone, and from 2 grams of the portion insoluble in alkali obtained 0.9 gram of benzoic acid, 1 gram of methyl propyl ketone, some halogenated oil and hydrochloric acid. The entire 2 grams is, therefore, accounted for. The formation of intermediate addition products was also demonstrated.

Pure mesityl oxide reacts so energetically with sodium that the products may even take fire with explosive violence; the sodium compound is so unstable that it cannot be isolated.

From the above considerations it is evident that the original descriptions of sodium acetone call for no change.²

¹ THIS JOURNAL, 19, 878 (1897).

² Since the above was written an article by Levi and Voghera (Gazz. chim. Ital. (1905), 35, 1, 277) has come to our attention. These investigators studied the electrolysis of KSCN, KI and NaI in acetone solution, water being rigidly excluded from their solutions. At the cathode, sodium-acetone and potassium-acetone respectively separated as white substances. With water these gave acetone and sodium or potassium hydroxides. The potassium-acetone gave 40.70 per cent. of potassium (calculated 40.62 per cent.), and dissociated, when placed in water, into acetone, potassium and hydroxyl ions, the correct lowering of the freezing-point for a molecular weight of 96 being obtained (found 95.3).

REVIEWS.

HANDBOOK OF METALLURGY. By C. SCHNABEL. Translated by H. LOUIS. Vol. II. London and New York: Macmillan & Co., Limited. 1905. Price, \$6.50.

Volume I. of Schnabel's¹ "Handbook of Metallurgy," translated by Louis, which covers the major non-ferrous metals, copper, lead, silver and gold, appeared in 1905 and was reviewed by the present writer.¹ The translation of the second and concluding volume, treating of the eleven minor non-ferrous metals—zinc, cadmium, mercury, bismuth, tin, antimony, arsenic, nickel, cobalt, platinum and aluminium—is based upon the second German edition, which appeared in 1904. The criticisms offered on Volume I. hold good for the present Volume II. To these may be added that, while American books on the four major non-ferrous metals, written by specialists, were on the market when Volume I. appeared, this is not the case with Volume II., if we except the standard work of Ingalls upon the metallurgy of zinc and cadmium. Volume II., therefore, is the only English book covering the field and will be welcomed by metallurgists and chemists, especially as the metallurgical practice of some of the minor metals in the United States is still in its infancy. Here the experience of Europe must form the basis of the development of methods suited to new economic conditions. The present second edition of 1907 has 841 pages, against 664 of the first edition of 1898, showing an increase of 177 pages. The larger part of these, 76 pages, is given to the metallurgy of zinc, mainly on account of the appearance of Ingalls's treatise; next comes nickel with 26 pages; then follows tin with 22; mercury with 18; and aluminium with 14; leaving 21 pages for the remaining six metals.

H. O. HOFMAN.

ÜBER MOHNBAU UND OPIUMGEWINNUNG. By H. THOMS. Berlin: Gebrüder Borntraeger. 1907. pp. 60.

In this monograph, which was published in the *Berichte der deutschen Pharmazeutischen Gesellschaft* the author gives a history of the culture of opium and its production. All countries of Europe, as well as the United States, have tried to raise opium, because of its remunerative qualities and its importance as a drug; but in all of them the project has been dropped because of the inability to compete with the opium of Turkey, India and Persia, on account of cheaper labor in the latter countries, and to the enormous variation in the morphine content

¹ THIS JOURNAL, 35, 473 (1906).

of the opium from year to year, due to variation in climatic conditions. A poppy field that yielded, in 1898, an opium containing 12 to 18 per cent of morphine, and was hence considered a very good opium, would in 1899 yield as much opium, perhaps, but the yield of morphine would fall to 5 per cent. In order to give the question a thorough trial, the author planted at Dahlem near Berlin, in Germany, poppy seed obtained from Turkey, Germany and Persia. The poppy plants bloom in the latter part of June and after ten days the unripe capsules or poppy heads are sufficiently developed to cut them with a sharp knife, so that each capsule receives six cuts across its side. The gum exudes and dries on the surface in globules which are scraped off next morning. The same capsules can be thus cut on three successive days before the yield of the gum begins to decrease, and for several weeks altogether before they cease exuding any gum. The German poppy plants matured much more slowly than the oriental plants, but developed into larger and sturdier specimens. It was found that, in the same soil, Smyrna poppy seed yielded in 1905 0.040 gram of dry opium per capsule, and in 1906, 0.034 gram of dry opium; German blue poppy seed yielded in 1905, 0.122 gram, and in 1906, 0.038 gram dry opium, and German white poppy seed yielded, in 1905, 0.141, and in 1906, 0.037 gram of dry opium per capsule. This showed the great variation in the yield when raised in Germany.

It further developed that the condition for the successful culture of opium is the amount of time necessary to obtain a definite amount of gum opium, or, in other words, the amount of labor necessary. Thus, to obtain 1 kilo of dry gum opium requires, in Germany, 283 hours. Based on German labor at 5 cents an hour this means that the opium raised in Germany would cost about \$6.50 per pound for labor alone. Gum opium sells to-day in New York at \$3.50 per pound. As labor in Asia, Persia or India costs about 1 cent an hour, the raising of opium in any country where labor is in demand is out of the question.

The author next considers the assay of opium, and doubts the correctness of standardizing opium by an assay for morphine alone, as is now generally the case in all countries. He bases this on the fact that the therapeutic effect of opium is not due solely to morphine, and that opium contains more codeine than has heretofore been considered to be the case. For the determination of morphine, the author gives a method based upon that of the Helfenberger *Annalen*, 1887, p. 37 and modified by Fromme¹ and himself. For determining

¹ Caesar and Loretz: "Gehaeftsbericht," 1906.

the narcotine, which has no medicinal value, he finds the method of Van der Wielen¹ the best, and for codeine he considers Chas. E. Caspari's method² the best.

He then publishes the results of the application of these assay processes to the opium he raised at Dahlem as follows:

Smyrna opium, 1905, contained 10.70 per cent morphine; 1906, 13.40 per cent morphine.

German blue seed opium, 1905, contained 10.59 per cent morphine; 1906, 11.12 per cent morphine.

German white seed opium, 1905, contained 10.87 per cent morphine; 1906, 10.84 per cent morphine.

Smyrna, 1906, contained 4.06 per cent narcotine and 1.13 per cent codeine.

Blue German, 1905, 1.90 per cent codeine and 1906, 1.32 per cent narcotine and 1.43 per cent codeine.

White German, 1905, 0.88 per cent codeine and 1906, 1.90 per cent narcotine and 1.59 per cent codeine.

Finally the author has assayed the unripe alongside of the fully ripe poppy heads or capsules and finds that the fully ripe capsules contain, contrary to general belief, quite a considerable amount of morphine, about half as much as the unripe, and, in addition, contain actually more codeine and narcotine than the unripe capsules, which latter are the only kind used at present in growing opium. In fact, the fully ripe poppy capsule contains, according to Thoms, about 2.5 times as much narcotine and codeine as the unripe capsule. As codeine is being used more and more in place of morphine, because it does not form the opium habit, this should be of value to all codeine manufacturers. The monograph is illustrated by some photographs of the poppy beds at Dahlem, showing them at various stages of growth and development.

A. R. L. DOHME.

THE ELECTROLYTIC DISSOCIATION THEORY. By PROF. R. ABEGG, PH.D., of the University of Breslau. Authorized translation from the German by CARL L. VON ENDE, PH.D., Assistant Professor of Chemistry, State University of Iowa. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1907. pp. 180. Price, \$1.25 net.

The scope of this little book can readily be seen from the Table of Contents. It comprises the following headings: Fundamental Conceptions of the Theory; Mobility of the Ions; Equilibria among Ions; The Dissociation Constant; Equilibria among Several Electrolytes, Hydrolysis, Avidity, Indicators,

¹ "Pharm. Weckblad," 1903, p. 189.

² "Pharm. Review," 1904, p. 348.

Heterogeneous Equilibria, Anomaly of Strong Electrolytes; Influence of Pressure and Temperature on Dissociation; Non-Aqueous Solutions; Chemical Nature and Ionization Tendency of the Elements.

The book deals with a number of the fundamental principles that underlie the theory of electrolytic dissociation, in a very elementary manner. It is well worth reading by any one who is just beginning his work in the field of physical chemistry.

The work of the translator, on the whole, seems to have been satisfactorily done.

H. C. J.

GLUES AND GELATINE: A PRACTICAL TREATISE ON THE METHODS OF TESTING AND USE. By R. LIVINGSTON FERNEBACH, Chemical Expert. Philadelphia, Pa.: D. Van Nostrand Co. 1907. Price, \$3.00 net.

Stripped of prolixity, this book is, in the main, a compilation of "Glue, Gelatine, etc." by F. Davidowsky; "Glue and Glue Testing" by S. Rideal, together with some recent articles in scientific journals, among which may be mentioned: "The Technical Examination of Glue."¹ "Notes on Glue and Glue Testing."² "The Grading and Use of Glues and Gelatine."³

No just credit has been given to the above authors, for there is no bibliography. It is true that the name of some author or scientific man is occasionally mentioned in connection with certain paragraphs, but, as there is no specific reference, the impression is given that the rest of the book is original. Some parts of it undoubtedly are original, as there are certain misstatements of facts, technical and commercial. Exploded laboratory experiments and rule-of-thumb opinions are stated with the solemnity used in announcing discoveries. Dealers in glue and gelatine are represented in the light of unprincipled sharpers seeking to cheat the consumer, whose salvation, perhaps, is a "chemical expert." The work should contain much that is novel and important to condone this affront to the industry.

The withdrawal of such books from circulation would probably save valuable time for those who might otherwise read them.

J. ALEXANDER.

¹ E. G. Clayton: *J. Soc. Chem. Ind.*, **21**, 690.

² H. J. Watson: *Ibid.*, **23**, 1189.

³ J. Alexander: *Ibid.*, **25**, 158.